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ABSTRACT

An independent Office of Technology Assessment (OTA) report of the deacidification program underway at the Library of Congress, this report was undertaken at the request of the House Appropriations Committee. Because of the particular concerns of engineering and safety which have been raised regarding this program, this report focuses on its effectiveness and safety, and compares the current program to other alternatives. The Library of Congress' program, which uses DEZ (diethylzinc) as a paper deacidifier, is discussed in detail, and the safety and environmental effects of this program are considered. The OTA findings suggest that more research and planning should be undertaken before embarking on a full-scale program using the DEZ process, and it is recommended that other alternative strategies be more fully explored. The text is supplemented by photographs, tables, and figures, and bibliographic notes/references are provided. (EW)

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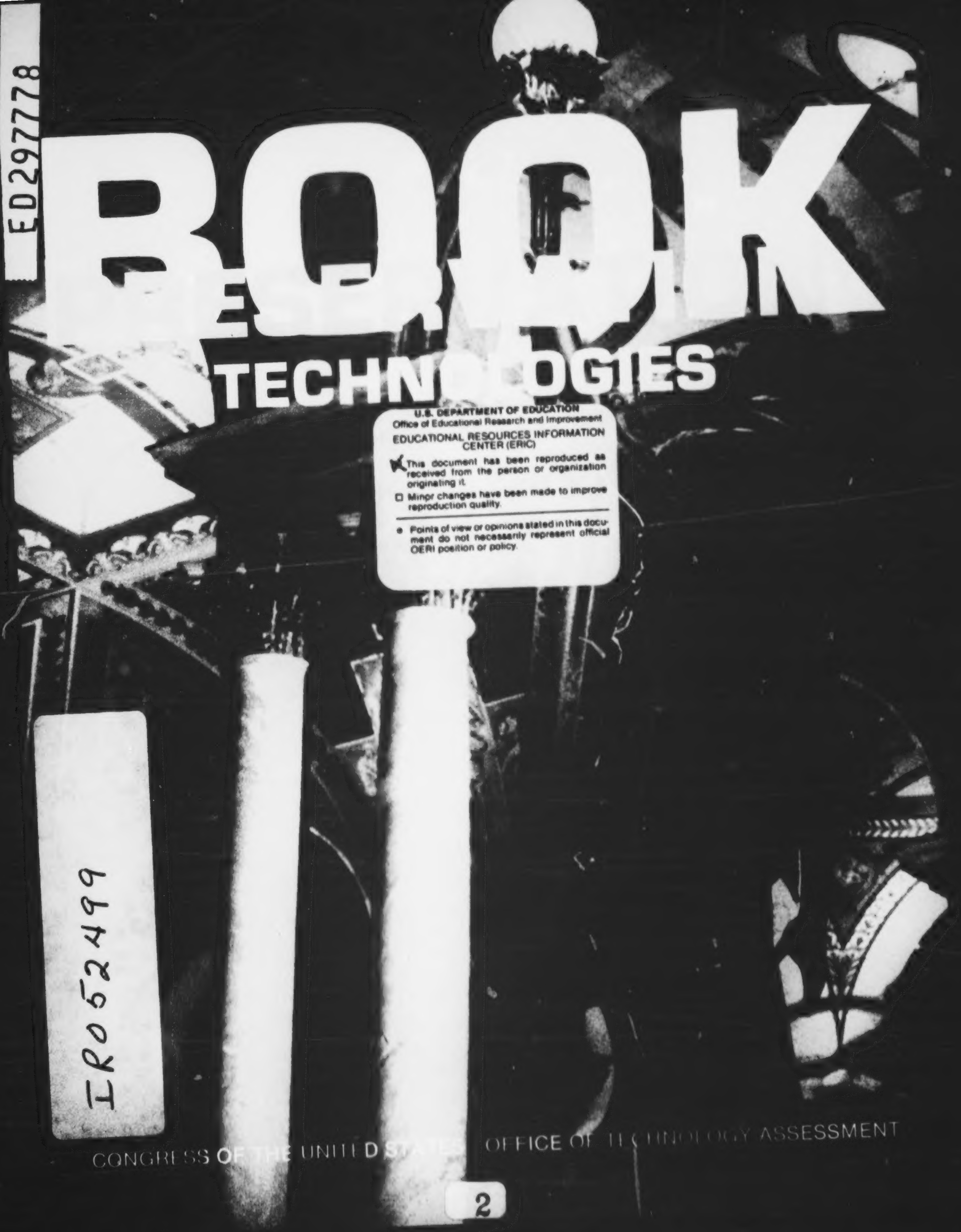

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Foreword

Even in today's high-tech society, books are the principal records of human civilization. Over the centuries, books have become the most reliable and permanent records available, but, in the last century, that reliability has been threatened by the use of "modern," acidic paper that becomes brittle and unusable in a relatively short time. Books printed since 1850 are deteriorating en masse in libraries the world over. Nowhere is this problem more severe than in the U.S. Library of Congress; a major preservation program addressing it was initiated in the early 1970s. The Library's mass deacidification process is now being tested at a pilot plant, and planning is underway to design and construct a full-scale facility that could treat about 1 million books each year.

This assessment analyzes the problem of acid deterioration of books and the program underway at the Library of Congress. The program at the Library involves the chemical treatment of books in a unique and effective process that, however, also presents some new engineering and safety concerns. Because of these concerns, the House of Representatives Committee on Appropriations requested this independent review of the Library's system and other available or potential processes. OTA has evaluated the Library's process and program with a focus on effectiveness and safety, and compared it to available alternatives. OTA has also developed information and analyses useful to other major libraries in the Nation that are faced with the same problem of preserving valuable books and papers.

OTA is grateful for the assistance provided by the assessment's advisory panel, workshop participants, and other consultants, and acknowledges the full cooperation of the Library of Congress in responding to requests for information, arranging meetings with its consultants, and reviewing materials. OTA also appreciates the efforts made by the developers of other deacidification processes to make available the most up-to-date information.

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NOTE: OTA appreciates and is grateful for the valuable assistance and thoughtful critiques provided by the advisory panel members. The panel does not, however, necessarily approve, disapprove, or endorse this report. OTA assumes full responsibility for the report and the accuracy of its contents.

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Introduction

PURPOSE OF THIS STUDY

Millions of books at the Library of Congress and other libraries around the world are deteriorating. Many books published since the mid-1800s are currently, or will soon become, too fragile to handle. The paper these books are written on becomes brittle over time and crumbles. The primary cause of this deterioration is acid. Chemicals used in the manufacture of paper from wood pulp, which stay in the paper, convert to a variety of acids and slowly destroy the strength of the paper's fibers over time. Other factors such as oxidation, varying or extreme temperature and humidity, exposure to light, air pollutants in storage areas, and the amount of use also contribute to the destruction of the books.

The Library of Congress has been working to solve the problem of acid paper in books since the early 1970s, developing a mass deacidification process that would inhibit the deterioration of book paper. About 25 percent of the 14 million books at the Library of Congress are too brittle for normal use. The main purpose of the Library of Congress program is to preserve and extend the life of paper materials before they reach this brittle, unusable condition. This would involve deacidification of new materials coming into their collection as well as existing materials not yet damaged beyond use.

Other libraries and researchers have also worked on this problem and small-scale processes are in use. The purpose of this assessment is to evaluate the appropriateness of the system under development by the Library of Congress and compare it to other available or potential processes. Although this report focuses mainly on the Library of Congress, it will hopefully assist the library community, in general, with decisions on how to cope with the acid book problem. Another recent report on this subject is titled "Mass Deacidification for Libraries" by George M. Cunha, published in *Library Technology Reports* of the American Library Association.

What Is The Library of Congress?

- The largest center for information storage in the world.
- Collections include 19 million volumes and 58 million pieces of stored data on phonograph records, motion picture reels, computer tapes, manuscripts, maps, prints, and photographs.
- Three Canons of Selection established in the 1940s to define the collections:
  - —materials necessary to the Congress and to the U.S. Government officers in performance of their duties;
  - —materials that express and record the life and achievements of the people of the United States; and
  - —records of other societies and peoples, especially those of most immediate concern to the people of the United States.
- Less than 25 percent of the collection is in English.
- Serves five audiences:
  1. Congress—Library provides research support, policy analysis, and training through the Congressional Research Service;
  2. professional library world—Library provides cataloging and other bibliographic services and leadership on library technology;
  3. executive agencies—Library provides information resources;
  4. scholars—Library provides research collections and support; and
  5. creative world—Library protects products and preserves traditions.

SOURCE: Charles A. Goodrum and Helen W. Dalrymple, *The Library of Congress* (Boulder, CO: Westview Press, 1982), p. 337.

THE ACID BOOK PROBLEM

The problem of acid deterioration of library books and other assets is not new. In 1898, an international conference was organized to discuss the poor quality and lack of permanence of paper made by recently developed wood pulping processes.[1] During the 1930s a number of researchers began to study the problem more systematically, establishing a correlation between the acid content of paper and its lack of permanence, and began experimenting with new papermaking processes for making acid-free papers. In the 1950s, the Council on Library Resources became a leading supporter for research on paper permanence, eventually leading to standards for permanent paper.

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[1] K.G. Schmude, "Can Library Collections Survive? The Problem of Paper Deterioration," *The Australian Library Journal*, vol. 33, No. 1, February 1984.

Although there has been an awareness of the problem for almost 100 years, a more global sense of urgency has only recently developed. The rapid increase in the size of library collections beginning in the late 19th century has created for the libraries and other institutions a crisis of enormous proportions that is now "coming of age."

How the Library of Congress Obtains Materials

1. *Copyright Office* receives about 130,000 books, 230,000 periodicals, and tens of thousands of sheets of music each year. It also receives maps, motion pictures, telephone directories, phonograph records, computer tapes, ballet notations, etc. All of these materials are received free of charge.
2. *Government Exchange* provides records of affairs from Federal, State, major cities, and foreign governments, as well as international government organizations. About 4 million publications are obtained through these channels each year. None of these materials are purchased. The Library obtains non-Federal materials by trading Federal publications.
3. *Gifts* include personal papers given outright or deposited with the Library. In 1980, about 1.8 million pieces were received.
4. *Purchased Materials* include:
    - newspapers—330 U.S. and 1,000 foreign;
    - foreign magazines—about 30,000;
    - foreign books—includes significant nonfiction and representative literature;
    - research materials for the CRS Library; and
    - blind and physically handicapped collection, this is the largest portion of the purchase budget, in 1980, about 1.9 million volumes were purchased for about $35 million.

SOURCE: Charles A. Goodrum and Helen W. Dalrymple, *The Library of Congress* (Boulder, CO: Westview Press, 1982), p. 337.

Although the materials and techniques used to make paper have changed, the underlying principles involved have changed little in 1,700 years. Materials containing cellulose (e.g., mulberry, flax, cotton, wood) are beaten and macerated in water creating pulp. The pulp is then formed in a mold and dried, leaving behind a mat of cellulose fibers. The water that remains after drying holds the matted fibers together. Additional substances are added in the processing that give paper its other familiar qualities. Sizing agents are added to reduce the penetration of liquids, making it possible to print without blotting. Fillers are sometimes added to make the paper whiter and opaque. Dyes, pigments, and strengtheners can also be added.

Paper can be extremely stable, maintaining its durability for centuries if taken care of properly. There are many examples of books published as far back as the 1500s that are still in fine condition. Paper permanence, the ability of paper to maintain its durability over time, has slowly declined over the years, however, to the point where we are lucky if the vast majority of "modern" papers, paper made since the mid-19th century last 50 years.

The more rapid deterioration of modern paper has been attributed to acids that accumulate in the paper. The source of the acids are chemicals that are either introduced during the papermaking process or are introduced subsequently from the environment. The acids attack the cellulose that makes up paper, breaking it into smaller and smaller pieces, until the paper has lost all of its durability.

Actually, the use of acid-producing materials in papermaking began as early as the late 17th century when European papermakers began to use alum (aluminum sulfate) in addition to animal gelatin as a sizing agent. Alum, in time, can be converted to sulfuric acid. Measurements of 400-year-old papers revealed that those with alum sizing have a higher acid content than those papers that just used animal gelatin or no sizing at all.[2]

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[2] W.J. Barrows Research Laboratory, Inc., "Permanence/Durability of the Book, Vol. VII: Physical and Chemical Properties of Book Papers, 1507-1949," 1974.

It was not until a series of innovations in the 19th century, however, that the acid content of paper rose dramatically. Alum-rosin sizing was introduced in 1803, replacing gelatin and gelatin-alum sizing. Alum-rosin sizing required excess alum, increasing the amount of this acid producing substance in the paper. In the mid-19th century, rags and linen were replaced by wood as the major cellulose feedstock. Wood pulp contains lignin and hemicellulose that easily breakdown in air, causing discoloration and forming acidic compounds. In addition, wood cellulose is more susceptible to acid reactions than the cotton cellulose derived from rags and linen. By the end of the 19th century, chemical wood pulping processes were developed to remove lignin (because of the discoloration it caused) but did so by using acidic solutions. As a consequence of these innovations, paper produced since the mid-19th century can have an acid content today 100 times greater than paper produced in the 1500s.[3]

The effect of this higher acid content can be devastating. In 1959, the William J. Barrow Research Laboratory, with support from the Council on Library Resources, measured the durability of books published in the United States between 1900 and 1949.[4] A 500-book sample was taken from libraries in and around the Richmond, Virginia area where the Laboratory was located. The study determined that 39 percent of the books published between 1900 and 1939 had already become very weak; the pages would crack after moderate use and would probably become too brittle to handle at all in another 25 years. Furthermore, another 49 percent of the books had a durability less than that of newsprint, the weakest paper used for printing.

Numerous libraries have sampled their collections and found the same sobering statistics (e.g., University of California, Yale, and Stanford). Yale's study concluded that 43 percent of the libraries' 9 million books are brittle and another 44 percent have a high acid content.[5]

The extent of the problem nationwide is staggering. The Association of Research Libraries (ARL) has estimated that 75 million books in the Nation's research libraries alone are endangered. Although many of these are still in print and can be repurchased by libraries, the ARL estimates that over the next 20 years, at least 3.3 million volumes must be transferred to another format if the the information they contain is to be saved.[6]

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[3] Ibid.

[4] W.J. Barrow, "Deterioration of Book Stock, Causes and Remedies," Randolph Church (ed.) (Richmond, VA: Virginia State Library 1959).

[5] Gay Walker, Head of the Preservation Department, Yale University Library, personal correspondence, July 10, 1987.

[6] Council on Library Resources, "Brittle Books: Reports of the Committee on Preservation and Access," Washington, DC, 1986.

APPROACHES FOR ADDRESSING THE ACID BOOK PROBLEM

Acid-Free Paper Production

The most obvious solution to the acid book problem is to make and use alkaline (acid-free) paper. New mass-producing technologies for such papers have been developed since the 1930s. Many university publishing houses now require the use of alkaline paper, and libraries have lobbied papermakers and publishers to move in this direction. However, there are a number of economic obstacles that impede the transition and it appears that only 15[7] to 25[8] percent of the book paper produced in the United States is alkaline. The prospects for producing more alkaline paper in the future will be discussed later in this report. Even if widespread use of acid-free paper occurred tomorrow, however, the problem remains of how to preserve the paper or the information that has already been accumulated.

Preservation Techniques

Libraries are no strangers to preservation. Over 40 institutions nationwide are actively pursuing

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[7] C.J. Shahani and W.K. Wilson, "Preservation of Libraries and Archives," *American Scientist*, vol. 75, May-June 1987, referencing R.G. Johnson, "U.S. Alkaline Fine Papermaking To Experience Slow But Steady Growth," *Pulp and Paper*, December 1986.

[8] "Report on Library of Congress Conference on Paper for Book Longevity," Library of Congress Information Bulletin, vol. 40, No. 13, Mar. 27, 1981.

How the Library of Congress Selects Materials

- About 10 million items are received by the Library each year, of these about 1.5 million items are selected for inclusion in its collections.
- Selection policies are based on subject matter, four levels of retention (i.e., comprehensive, research, reference, minimal), specific decisions about a subject and specific decisions about individual items.
- Routine selection involves review by about 30 specialists. About 30 other people are involved in processing the book and getting it onto the shelves.
- Most domestic books are obtained through the Copyright Office. The Library retains the majority of hardback books, a sampling of paperbacks, and many college textbooks. Almost no texts for elementary or high school are retained.
- Most foreign books are selected after purchasing the same publications as the largest library in the country or by working with a single dealer in a particular country.

preservation programs,[9] spending millions of dollars each year. The national libraries and archives of many other countries are also actively engaged.

Preservation involves a wide range of activities, including the general conservation of important and rare books and documents, environmental control, and the training of staff in proper storage and handling procedures. Many techniques have been developed and are in use today. Aside from the environment control techniques and general handling and storage procedures, many of these techniques are essentially manual operations performed one page at a time, are very time-consuming, and often require skilled practitioners. The size of the acid book problem now and in the future, however, dwarfs the current efforts and will require adapting existing techniques or developing new ones.

There are two aspects to dealing with the acid book problem—preserving the information that exists on materials that have already become brittle, and preserving those materials that have not yet become brittle. This study will focus on deacidification of materials before they become brittle and will *not* cover the technologies or techniques that have been developed to transfer the information to another media or format. However, a short discussion on paper strengthening follows here.

Strengthening

In cases where it is desirable to maintain the original format, embrittled materials can be handled by laminating or mounting. An early technique for laminating brittle paper was to sandwich it between finely woven silk, using starch or paraffin as an adhesive. During the 1930s, the National Bureau of Standards developed a technique that sandwiched brittle paper between two sheets of cellulose acetate, the cellulose acetate was bonded to the paper by heating and pressing. The Library of Congress developed a technique that encapsulates the paper between two sheets of polyester film (e.g., mylar).[10] The film is bonded around the edges but is not bonded to the paper, therefore, the technique is reversible.

Although these techniques can be automated to some extent, they can only be done a single sheet at a time. Books would have to be unbound and then rebound. Costs are high and the process is usually limited to preserving rare books.

New techniques are being developed that would actually strengthen the paper by polymerization. This essentially reverses the breakdown of cellulose fibers by forming physical links between the broken cellulose fibers, restoring the paper's flexibility. Of course, this is a short-term solution for acidic papers unless deacidification is also part of the treatment.

Deacidification

For materials that have not yet become brittle, techniques have been developed to neutralize the acids that cause the paper to deteriorate and to deposit an alkaline buffer that acts as a reserve to neutralize any acids that may continue to form. The objective is to extend the life remaining in the pa-

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[9] "Millions of Books Disintegrating in Nation's Libraries," *Anderson Daily Bulletin*, Oct. 23, 1986.

[10] C.J. Shahani and W.K. Wilson, "Preservation of Libraries and Archives," *American Scientist*, vol. 75, May-June 1987.

Photo credit: Library of Congress

Manual book deacidification technique treats one page at a time.

per at the time it is treated. The history of the development of single sheet, spray and mass deacidification techniques, including the contributions of the William J. Barrows Research Laboratory, are described in greater detail in other documents.[11]

Most of the deacidification techniques in use today are manual liquid solution processes. Sheets of paper are either dipped in or sprayed with a solution containing one or more alkaline compounds. The compounds precipitate out of solution, neutralizing the acids. Excess precipitate is deposited as a buffer. The alkaline compounds are normally magnesium or calcium carbonates and the solvents can be aqueous or non-aqueous.

Current manual techniques are time-consuming and expensive. The paper must be treated one page at a time. Books must be unbound if they are dipped into the solution. Each page must be tested to make sure that inks, colors, etc. are compatible with the solvents being used. Some solvents not only dissolve the alkaline compounds used to neutralize the acids but will also dissolve certain inks and pigments and other book materials. These processes are painstaking operations and demand highly skilled practitioners. They are normally used only for rare books where the value of maintaining the original format is greater than the cost of treatment.

The lack of financial resources, time, and manpower make it impossible for most of these preservation processes to be of much use in tackling the more general acid book problem. Over the last 10 to 15 years, mass deacidification techniques have been under development that would treat many books at once. Such techniques would not only increase the number of books that could be treated, from tens of thousands to hundreds of thousands if not a million books per year, but would also lower the cost of treatment per book.

Estimated processing costs for various mass deacidification techniques currently under development range from $2 to $6 per book. These estimates, however, typically do not include the initial capital investment costs (which can be quite substantial) or the costs associated with handling large volumes of books. Book handling will also present a variety of technical and logistic problems that must be considered. Nevertheless, preservationists are looking forward to the development of cost-effective mass deacidification processes.

There are two mass deacidification systems in operation in North America (one at Princeton University and one at the Canadian National Library and Archives) and a few under development (one of these is the Library of Congress' system). Some processes are also under development in Europe.

The two operating systems use the non-aqueous liquid solution developed by Wei T'o Associates. Princeton University uses Wei T'o spray and has developed a semi-automated system. Books are

Photo credit: Library of Congress

Wei T'o deacidification system used at the Canadian National Library and National Archives.

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[11] See C.J. Shahani and W.K. Wilson, "Preservation of Libraries and Archives," *American Scientist*, vol. 75, May-June 1987, pp. 240-251; and George M. Cunha, "Mass Deacidification for Libraries," *Library Technology Reports*, May-June 1987, pp. 363-477

treated one at a time in an exhaust hood. The pages are turned manually while an automated spray moves back and forth across the page. The system treats about 1,000 books per year. The Canadians are using a system developed by Wei T'o Associates. Ten to twenty books are placed in a chamber which is then filled with the deacidifying solution. The system was built as a pilot plant to test its feasibility; however, the National Library and National Archives of Canada are now using it in production, treating about 40,000 books per year. A process developed by the Bibliotheque Nationale in France is very similar to the Canadian system and began operations during the fall of 1987.

The Library of Congress is developing a vapor phase process which is the main subject of this report. A pilot plant capable of treating 300 books at a time has been built. Tests on the system began in 1987. Another process under development is called the "Bookkeeper." Originally developed by the Koppers Co., Inc., the process uses a dispersion to deposit ultra-fine alkaline particles. A pilot-scale system has been designed and awaits demonstration. As this report was being written, another firm proposed a new vapor phase process. OTA has collected available information about all of the processes and has evaluated their relative advantages and disadvantages.

Combined Strengthening/Deacidification

Deacidification techniques are effective for books and paper that are not yet brittle. They cannot, however, restore lost durability. An ideal tool for the preservationist is a process that both deacidifies and strengthens books en masse. It would be very desirable to combine the deacidification processes under development with the strengthening techniques that are also being developed. Such techniques are under development in Europe.

One combined strengthening/deacidification process is operating (at a very small scale) and two are under development. The Austrian National Library has a small-scale system to treat its newspaper collection using an aqueous process with calcium hydroxide for deacidification and methyl cellulose for strengthening. The German Library in Leipzig is developing a different strengthening process using this same aqueous deacidfication chemistry. Strengthening will be accomplished by depositing a new layer of paper composed of cotton cellulose fibers. The British Library has begun development of a polymerization process for strengthening. Depending on the chemical used, the process could also be used to deacidify. None of these combined processes have been developed far enough to be considered for mass book preservation in the near future.

FINDINGS

The Library Process and Program

The Library of Congress has recognized the problem of acid deterioration of books and other paper materials for a long time. The Library staff have invested considerable effort in the investigation of deacidification processes and have selected the DEZ process as the one that meets their needs. Selection of the DEZ process by the Library of Congress has followed a logical procedure comparing alternatives on the basis of criteria established by the Library for its collection. **Since the late 1970s decision to pursue the diethylzinc (DEZ) process, most of the Library's effort has been devoted to perfecting this process and solving the engineering, safety, and other problems associated with the chemical treatment plant.**

The Library of Congress has built a second DEZ pilot plant and has begun a series of engineering and process effectiveness experiments as of this writing. The Library staff have done early planning but have not made firm decisions yet about the management, design, construction, and operation of a full-scale facility. A total system including book selection, handling, and transportation is planned, but has yet to be designed. Final plans for contracting and management of the full-scale plant also are needed. **The Library of Congress needs to consider important details of project planning and manage-**

ment soon in order to more accurately predict costs, capacity, and operational results of this major undertaking.

Technological Effectiveness

The DEZ process developed by the Library of Congress extends the life remaining in the paper at the time it is treated. The Library claims that the process will extend the life of acid book paper three to five times its life if left untreated. These claims are based on fold endurance tests that have been made on a variety of test papers. **But it is not clear how long the life of an actual book in the Library's collection will be extended.**

The Library intends, as part of its current pilot-plant tests, to analyze the overall benefits to all books to be expected with DEZ treatment. **The results of those tests are needed to quantitatively project the benefits of the entire program.** Some scientists would also urge more tests on older papers typical of the Library's collection.

Safety

DEZ is a hazardous substance that must be handled carefully and in accordance with strict safety procedures. DEZ will spontaneously ignite if exposed to air. Fire is the principal hazard, and there is a remote chance of explosion. **However, DEZ has been used safely for other purposes.** There is no unusual fire hazard, however, once the books are treated.

The early engineering development of the DEZ process by the Library and NASA Goddard resulted in an accident caused by inadequate management of engineering and safety procedures. Careful attention to safety and good chemical process engineering standards have been followed with the design, construction, and plans for operation of a second pilot plant with Texas Alkyls in Houston. **OTA finds these initial efforts adequate, but pilot plant tests now underway are needed to demonstrate all safety aspects. As of this writing a series of engineering experiments is underway at the Houston pilot plant.**

The full-scale plant, if built, will need equal or greater engineering attention, especially related to safety standards and practices during operations. Scale-up design will encounter additional engineering problems. Safety practices must be developed for a new site, new plant management, new operators, and a new community setting.

Cost

To accurately and completely define costs, capacity, and operations for a full-scale DEZ facility, some basic decisions and plans remain to be made. These plans include a total system design, including not only the full-scale DEZ facility but also the procedures for book selection, handling and transportation, and final plans for contracting and management.

For the purpose of this OTA study, the Library of Congress estimated the capital cost of the full-scale DEZ deacidification facility at $4.9 million without a contingency and the annual operating costs for a capacity of 1 million books per year at $1.8 million. These costs do not include a number of items that have not yet been detailed enough to make estimates (e.g., book transportation) or are not considered now by the Library to be applicable (e.g., engineering development at the pilot plant). **OTA considers that actual costs could vary considerably from these estimates once the important engineering and planning decisions listed above have been made.** OTA also believes it useful to add rough estimates of the missing items and contingencies for unknown factors and thus arrive at a more inclusive budgetary estimate.

The most critical factor in per-book costs is the capacity of the final plant. The vacuum chamber cycle time has a major influence on capacity as do transportation and book handling factors. These latter parts of the system need to be defined. Costs for transportation and handling are also very rough at this time. OTA has attempted to factor in these uncertainties to arrive at its own estimate. OTA has also used a ±20 percent range of numbers because of the uncertainty of these costs. OTA's resulting *per book cost estimate is from $3.50 to $5.00* including amortization and interest on capital assuming a 1 million books per year plant capacity.

Alternative Processes

Although the problem of deteriorating paper has been known for almost 100 years, **only one mass deacidification plant has been operating anywhere for any length of time**. The Wei T'o process has been used by the National Archives of Canada for the past 7 years at a capacity of about 40,000 books per year. There are no deacidification facilities that can handle the large number of books (over 1 million books per year) envisioned for the Library facility. Other systems are in operation at a much smaller scale, are designed for a pilot plant scale, or are only ready for testing on a pilot plant scale.

Of those processes for which OTA had sufficient data, two of them, Bookkeeper and Wei T'o, merit some consideration as alternatives to DEZ.

In general, the effectiveness of deacidification processes has not been unambiguously established. OTA has found no independent tests and ev
tions of the Wei T'o and Bookkeeper processe
data on treatment results have been developed by the firm or organization that is promoting the process. This is also true of the Library of Congress. (However, the Library of Congress' Laboratory is highly regarded as a leader in the field and tests of DEZ treatment effectiveness are far more extensive than those conducted on the alternative processes.) **Without some independent tests with standard procedures, comparisons of the final results of alternative processes will always be uncertain.**

By comparision to Bookkeeper and Wei-T'o on a pilot plant scale (50 to 150 books per day), the Library of Congress' pilot plant at Texas Alkyls appears to be considerably more expensive. **Whether the cost difference would be significant for a larger scale cannot be determined without further pilot plant tests (not yet done at all for Bookkeeper) and complete design for the large-scale plant.**

ORGANIZATION OF THIS REPORT

The remainder of this report is presented in two parts. Part I addresses the Library of Congress' program for mass deacidification of books and other library materials. It analyzes the work completed to date and the specific plans to build and operate a large-scale chemical treatment plant over the next few decades. That plant is expected to deacidify over 1 million books per year.

Part II addresses possible alternatives to the proposed Library of Congress' deacidification system and other issues related to the value of deacidification and the costs and results of other approaches. This part includes discussions of acid-free paper production; the effectiveness and costs of competing processes; and an evaluation of chemical treatment results to be expected.

Part I

The Library of Congress' Mass Deacidification Program

Chapter 1

Overview

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Chapter 1

Overview

INTRODUCTION

Libraries around the world are faced with a serious preservation problem but it is of huge proportions at the Library of Congress. The Library houses over 66 million items, including 14 million books. It is estimated that 25 percent of these books are brittle and another 1 to 2 million are at risk of becoming brittle over the next 20 years. As a major part of the their overall preservation effort, the Library initiated a program aimed at deacidifying books en masse. Much of that program has been devoted to the development of a process capable of treating between 500,000 to 1.5 million books per year. The process is unique and has many advantages over more traditional techniques. However, there have been questions raised about the process' effectiveness, safety, and costs.

Photo credit: Library of Congress

Brittle book from the Library of Congress' collection.

Part I of this study will evaluate the Library of Congress' mass deacidification program and the issues of effectiveness, safety, and cost in an effort to assist Congress with its decision about authorizing this program to proceed.

LIBRARY OF CONGRESS' PROBLEM AND STRATEGY

The Library of Congress' holdings of over 66 million items ranges from books to maps to musical scores. Books comprise the single largest holding. The Law collection and the General collection contain almost 14 million volumes, and receive over 350,000 additional books each year. In addition to books, the Library holds over 1 million technical reports, 35 million pages of manuscripts, over 3 million sheets of music, and nearly 4 million maps (see table 1). All of these items are at risk of becoming brittle and most are potential candidates for treatment.

In January 1984, the Library sampled the books in their Law and General Book collections to determine how many books were already brittle and how many had high acid content and, therefore, were at risk of becoming brittle.[1] Based on this sample, the Library estimated that 25 percent of their collection, over 3 million volumes, had already become too brittle to permit circulation (see figure 1). The pages of these books cracked when folded. Another 45 percent of the books were categorized as weak (i.e., their pages on the average could not withstand 50 folds). Of the collection, 97 percent are acidic (a pH value less than 7.0), and, therefore at risk of becoming brittle (see figure 2). Roughly 50 percent of the collection is made with paper containing lignin (see figure 3). Lignin is a highly unstable constituent of wood pulp and leads to rapid deterioration of paper. The Library estimates that each year over 77,000 additional books become too brittle to circulate.[2] It should also be noted that the median age of the books in this collection is 25 years.

---

[1] *The Design and Analysis of a Sample of the Condition of Books in the Library of Congress*, a Report prepared for the Library of Congress by King Research, Inc., Mar. 28, 1984.

[2] "Congress Considers 'Brittle Books'," *Publisher's Weekly*, March 1987, p. 13.

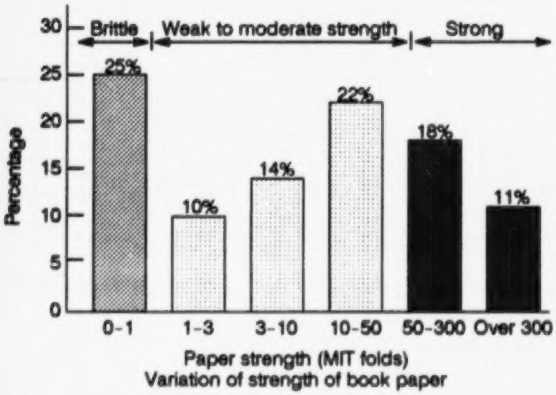
Table 1.—Library of Congress Collections on Paper As of Sept. 30, 1986
(numbers rounded to nearest thousand)

	Collection	Volumes	Sheets
DEZ treatment expected	Regular books	14,046,000	
DEZ treatment planned	Manuscripts		35,522,000
	Maps		3,862,000[a]
	Sheet music		3,699,000
DEZ treatment considered	Other printed materials		6,647,000[a]
	Technical reports	1,414,000	
	Art books	348,000	
	Music manuscripts		319,000
	Prints and drawings		257,000
	Pamphlets		179,000[c]
	Popular applied graphic arts		95,000
	Posters		61,000
No DEZ treatment	Rare books	594,000	
	Fine prints		95,000[b]
	Bound newspapers	40,000	

[a] Includes some volumes.
[b] Includes some portfolios.
[c] Mostly booklets.

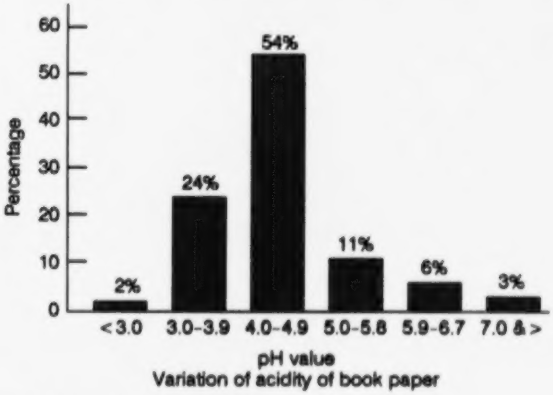
SOURCE: Library of Congress.

Figure 1.—Library of Congress General and Law Collections Survey of Paper Strength



SOURCE: Library of Congress, January 1984.

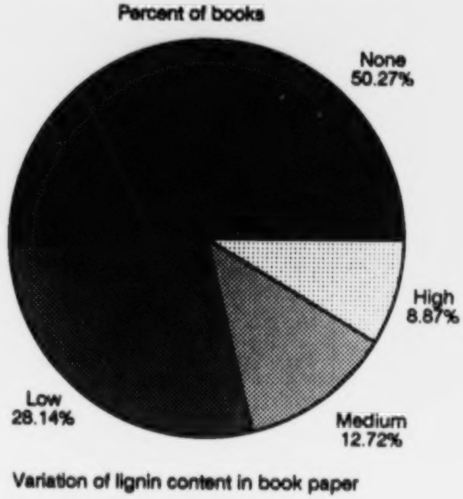
Figure 2.—Library of Congress General and Law Collections Survey of Paper Acidity



SOURCE: Library of Congress, January 1984.

In an effort to preserve their collection, the Library operates a comprehensive preservation program which includes rare book and document conservation, extensive environmental control, microfilming, book binding, and new optical disk formatting. Microfilming represents a major part of the preservation effort devoted to transferring information from brittle materials. Besides maintaining the newspaper collection on microfilm, the Library also microfilms between 10,000 and 20,000 brittle monographs and serials per year at a cost of about $40 per volume. It is the largest microfilming operation in the world. Even so, they cannot keep up with the number of books that are deteriorating. With 3 million books already brittle and 70,000 additional books becoming brittle each year, the Library's stacks will hold about a 200-year backlog of brittle books by the year 2000.

Figure 3.—Library of Congress General and Law Collections Survey of Lignin in Paper



SOURCE: Library of Congress, January 1984.

To slow down the embrittlement of acidic books, the Library decided to develop a mass deacidification process that would run in parallel with the microfilming program. It is important to note that deacidification is not an alternative to microfilming but a complimentary treatment that delays the need to transfer information to a new media. Deacidification by itself, i.e., without parallel strengthening, cannot help the 3 million books that are already brittle.

The basic strategy of the deacidification program is to treat all new aquisitions entering the collection first, before putting them into the stacks. In addition, books already in the collection would be selectively deacidified over time. The Library set a goal of deacidifying their entire book collection in 20 years.

The rationale for treating the incoming books first is that it should increase the cost-effectiveness of the program. Deacidification is generally believed to extend the life of a book by two to five times. Therefore, if paper in a new book has 50 years of useful life remaining, deacidification can extend this to 100 to 250 years. If paper in an old book has only 5 years of life remaining, deacidification will only extend its life 10 to 25 years.

The Library also wants to be able to treat other formats, and has expressed intentions of experimenting with adding a strengthening step to the process.

STATUS OF THE DEACIDIFICATION PROGRAM

The Library began its mass deacidification program in 1973. The program now consists of four basic subprograms:

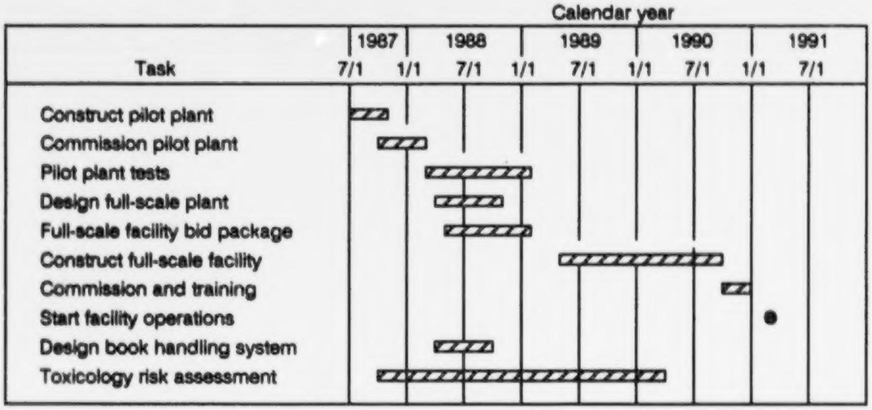
- the development of the plant engineering and large-scale facility for the mass deacidification process;
- the development of an appropriate quality control program;
- the development of a book handling management program; and
- an assessment of the health and environmental impacts.

A master schedule for the program is shown in figure 4.

Process Development

Most of the effort to date has focused on process development. Beginning in 1973, the Library's chemists explored various ideas in mass deacidification and invented a unique process utilizing diethylzinc (DEZ) vapors. Numerous laboratory and large-scale tests have been conducted to verify and develop the process. Currently, a pilot-scale system (capable of treating 300 books at a time) has been designed and constructed at Texas Alkyls, outside Houston. Texas Alkyls is the principal manufacturer of DEZ in the United States and has been working with the Library since the beginning of its program.

Figure 4.—Library of Congress, Mass Deacidification Program: Current Schedule of Major Tasks, January 1988



SOURCE: Office of Technology Assessment, 1988; based on information received from Library of Congress.

This is actually the second pilot plant that has been built by the Library. The first was designed, built, and operated by Northrup Services, Inc., on site at NASA's Goddard Flight Center in Greenbelt, Maryland. This plant was demolished in 1986 after two fires and an explosion rendered it inoperable. DEZ is pyrophoric, i.e., it will spontaneously ignite in air. Therefore, fire is a hazard that must be safely managed. This issue will be more fully discussed in chapter 5.

Construction of the Texas Alkyls pilot plant was completed in October 1987. The first tests of the plant began in December 1987.

The Library has contracted with Texas Alkyls to run 10 to 15 tests during 1988. These tests will evaluate the system's operability, effectiveness of treatment, safety, and economics. They will also be used to optimize the process parameters, cycle times, and final design (including plant capacity), for a full-scale system.

The full-scale plant is scheduled to begin construction in 1989 and to begin operation in 1990-91. The plans for who will design, construct, manage, and operate the plant have not yet been determined. The option that has received the most attention is to locate the plant at Fort Detrick in Frederick, Maryland. Under this option, the U.S. Army Corps of Engineers would contract for the design and manage the construction of the plant. The Library has stated its interest in contracting the management and operation of the plant to a private chemical company that has had experience in handling materials such as diethylzinc.

Photo credit: Library of Congress

Books prepared for DEZ treatment experiments with weigh cells and thermocouples at Texas Alkyls pilot plant.

Quality Control

A quality control program is being designed to ensure that the effectiveness of the process is maintained. As of January 1, 1988, test criteria had been proposed that include accelerated aging/fold endurance tests and analysis of the following major factors:

- completeness of deacidification,
- average percent zinc oxide deposited,
- uniformity of zinc oxide deposited,
- cover stains,
- text block rings,
- odor, and
- other.

Tests at the Texas Alkyls pilot plant are planned to provide information so that a statistically validated quality assurance program can be developed. The most important issue that will be addressed is the evaluation of test books as surrogates for actual books in the Library's collection. This evaluation will include data on suitability of various test papers, correlation of test book characteristics with regular books, and determination of a dose-response curve for test papers and its correlation with regular books. If test books do not provide a suitable surrogate for actual books, then an alternative approach will be necessary. A consultant to the Library has suggested using purchased used books to represent books already in the Library collection and extra copies of new books that are to be treated.

Another issue that will be addressed is the appropriate number, format, and placement in chamber of test books.

The pilot plant tests to develop a quality control program will also provide a large reservoir of treated books of known characteristics and composition for research purposes; and data to correlate new test paper behavior with that of papers previously used but now unavailable.

Book Handling

Book handling and its management represents a major part of the deacidification program. This part of the program has been divided into three integrated projects:

- the movement of books between the Library and the treatment facility,
- the procedures for returning treated books to circulation at the Library, and
- coordination with other preservation programs.

Photo credit: Library of Congress

First prototype of book handling carts for DEZ treatment.

The movement of books involves both logistics and design. The Library has experience in moving tens of thousands of books each year, but not a million books each year. Loading docks must be redesigned, and equipment including fork lifts, carts, etc., must be designed to operate in relatively confined spaces. The obsolete loading dock at the Jefferson Building has been redesigned by an outside consultant and construction work is to begin in 1989. The Library has also contracted with an outside firm to study the design of book-handling equipment and logistics.

The procedure for returning treated books to circulation basically requires some form of identification that the book has been deacidified. Logistics and the design of that identification system are considered very important by Library and preservation specialists. These topics will be addressed by the aforementioned study.

The Library has three ongoing preservation activities that also involve pulling books from the stacks for treatment of some kind. In addition to microfilming, the Library has relabeling and rebinding programs. Currently, these programs are not coordinated and books are selected independently from the collection. However, these programs will have to be coordinated with the mass deacidification program to ensure an efficient operation. The coordination between microfilming and deacidification is the most problematic. Deacidifying a brittle book is not cost-effective. However, the number of brittle books that would be pulled from the shelves would quickly overwhelm the microfilming capability of the Library. The costs associated with storing and managing a separate inventory of brittle books while they await processing may be prohibitive. The Library staff is still discussing this issue.

Book handling is a critical factor in any large-scale deacidification program. It may actually limit the eventual capacity of the deacidification system and, although only rough estimates have been made, OTA believes it could represent a major operating cost.

Health and Environmental Assessment

The Library has completed some limited laboratory toxicology studies and extensive literature studies on the health effects of treated books on library workers and users. The major change imparted to books during the treatment is the deposition of zinc oxide in the paper. In general, zinc oxide is considered a benign substance. However, the effects of exposing the skin to treated papers or ingesting treated papers orally were examined on mice and rabbits. No adverse effects were identified. The Library has also designed an extensive animal study to examine the effects, including carcinogenic effects, of chronic inhalation of the dust that may be associated with the process or the treated paper. The study was begun in 1987 and will take at least 2 to 3 years to complete.

The Library also intends to assess the environmental impact of the full- scale plant. The Library did make an earlier preliminary assessment, during the design of the first pilot plant, but this must be redone to take into account the new design. Who will perform the new assessment, and in what detail, will be determined after the design and operations planning for the full-scale plant is completed.

Funding

The Mass Deacidification Program is a line item in the Library's budget. Since the beginning of the program in 1973, the Library has spent $4.5 million on process development. Design, construction, and testing at the Texas Alkyls pilot plant has cost $2.8 million. Additional funds have been spent on designing and planning for the book handling managment. The animal study will cost about $1.5 million.

The Library, at the request of OTA, has estimated the capital and operating costs for the full-scale plant assuming it will be placed at Fort Detrick. These costs were estimated (by Library engineers working in conjunction with the pilot plant design team and architects working on the full-scale design) at $4.9 million to build and $1.8 million per year to operate at a capacity of 1 million books per year. OTA added a rough estimate of certain costs not included in the above figures and concluded that total capital costs may be $11.1 million for the facility and total annual operating costs may be $2.8 million.

DISCUSSION

The Library of Congress has recognized the problem of acid deterioration of books and other paper materials for a long time. It has invested considerable effort in the investigation of deacidification processes and has selected one process that best suits its objectives.

The Library's strategy is to deacidify all new books as they enter the Library (about 350,000 per year). In addition, the Library plans to treat the rest of its book collection over a 20-year period. Deacidifying old books, without strengthening, may not be as cost-effective as doing both—i.e., deacidification and strengthening. The Library intends to incorporate strengthening into its program at some future time, but has not yet selected an approach to do so.

Selection of the DEZ process by the Library has followed a logical laboratory routine in comparing alternatives on the basis of criteria established by the Library for its collection. However, since a decision to pursue the diethyl zinc (DEZ) process in the late 1970s, the Library has directed very little effort toward supporting the development or testing of other alternatives. The Library has investigated and kept informed of other paper preservation work in the United States and abroad, however, most of its effort has been devoted to perfecting the DEZ treatment process and solving the engineering, plant safety, and other problems associated with the DEZ chemical treatment plant.

The Library of Congress has built its second DEZ pilot plant and has begun a series of engineering and process effectiveness experiments as of this writing. It has done early planning but has not yet made firm decisions about the management, design, construction, and operation of a full-scale facility. A total system design would include book selection, handling and transportation, and procedures for contracting and management of the full-scale plant. The Library of Congress needs to consider important details of project planning and management soon in order to more accurately determine costs, capacity, and operational results of this major undertaking.

Chapter 2

The DEZ Process and Its Development

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Chapter 2

The DEZ Process and Its Development

INTRODUCTION

This chapter briefly describes the DEZ process and its evolution. OTA finds that the evolution has followed a reasonable path from laboratory to pilot plant demonstration. However, OTA is conducting its evaluation in the middle of ongoing development efforts and there are a number of engineering issues that remain to be solved, including how the Library will scale-up to a full-scale facility.

THE DEZ PROCESS

General Description

The mass deacidification process that the Library has been developing uses DEZ vapors to treat books. DEZ belongs to a class of compounds called metal alkyls or organo-metallics. Metal alkyls, in general, and DEZ in particular, will react very quickly with free hydrogen ions. Therefore, acids, being generous donors of free hydrogen ions, will react very quickly with DEZ. Deacidification occurs as DEZ vapors permeate the books and react with all acids in the paper converting them to zinc salts.

DEZ vapors also react with water in the paper to form zinc oxide. The zinc oxide acts as an alkaline buffer that can neutralize any acids that may form after treatment. The amount of zinc oxide that gets deposited depends in a large part on the amount of water in the books. It also depends on the amount of the DEZ used, time or rate of exposure, and particular permeability of the paper.

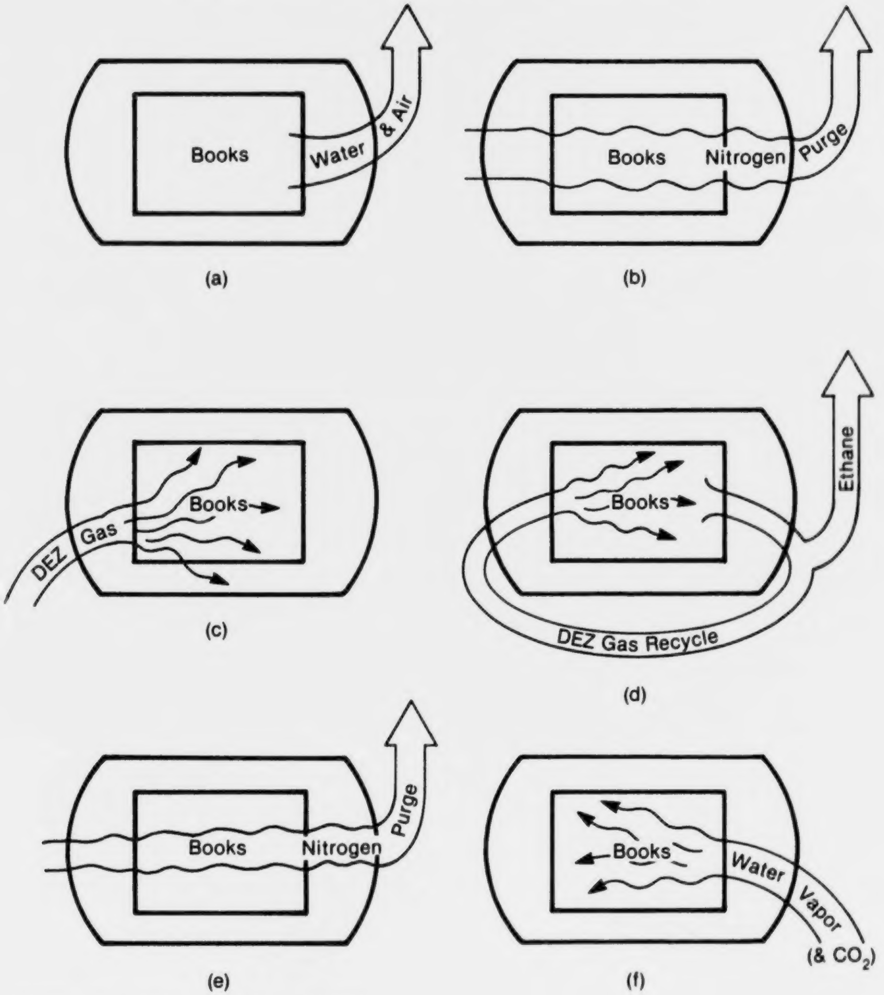
The process basically consists of three steps; dehydration, permeation, and rehydration. Dehydration reduces the amount of water in the books to some predetermined amount based on the amount of zinc oxide that is desired. Permeation exposes the books to the DEZ vapors. Rehydration soaks the books in water vapor to restore moisture to the books. An optional step during rehydration is to soak the books in moist carbon dioxide. This option will be discussed more fully later in this chapter.

Metal alkyls are pyrophoric, meaning they will spontaneously ignite if they come in contact with air. Therefore, the book treatment process must take place in an air-free environment within a vacuum chamber. The Library process uses DEZ as a gas only at very low pressure within the vacuum chamber.

The following is a general description of the process as it has evolved to date:

> Books are placed in a processing chamber. The air in the chamber is removed through a vacuum pump, lowering the pressure inside the chamber. The chamber is kept at a low pressure while the books are heated. Water migrates out of the books and evaporates. The evaporated water is removed through the vacuum pump. The amount of water removed is monitored indirectly by measuring book temperatures (see figure 5a).
>
> Once the desired amount of water has been removed, the chamber is purged with nitrogen gas to ensure that no air remains in the chamber (see figure 5b).
>
> After the chamber is purged, DEZ vapors are introduced into the chamber. DEZ vapors react with the acids and water in the books generating both heat and ethane gas. Exposure to the DEZ vapors continues until no more heat or ethane are evolved or until the desired amount of zinc oxide has been deposited. The amount of zinc oxide that has been deposited can be monitored indirectly by measuring book temperatures (see figure 5c).
>
> Ethane gas and unreacted DEZ vapors are removed from the chamber. The unreacted DEZ is condensed and recycled. The ethane is vented to the atmosphere (see figure 5d).
>
> When the permeation step has been completed, the chamber is again purged with nitrogen gas to ensure that all of the ethane and unreacted DEZ is removed (see figure 5e).
>
> After the chamber is purged, water vapor (or moist carbon dioxide) is introduced into the cham-

Figure 5.—Key Steps in the DEZ Treatment Process



SOURCE: Office of Technology Assessment, 1988.

ber. The books are allowed to soak in the water vapor until much of their original moisture content is restored. The amount of moisture taken in by the books is estimated by monitoring water introduced (see figure 5f).

When the desired amount of moisture has been restored, the chamber is vented to the atmosphere and opened and the books removed.

Process Control

Physical and chemical events during processing with DEZ occur over a relatively wide range of temperatures and pressures. Therefore, fine control of these parameters is not needed except to optimize the process. However, there are a few critical temperatures and pressures that do impose limits on the process. Thus the temperatures and pressures must be accurately monitored and measures must be incorporated to control them.

During dehydration, the books will lose heat. The book temperature must be controlled to prevent them from freezing and to keep cycle time short. Also during dehydration, it is undesirable for the water vapor in the chamber to condense, therefore, the interior surfaces in the chamber must be kept above the dew point temperature of water.

If the water does condense and remains in the chamber as a liquid it will react with the DEZ vapors during permeation and will foul the chamber with excess zinc oxide and will waste DEZ. If liquid DEZ should somehow enter the chamber during permeation and there is liquid water present, there will be a vigorous reaction, generating excess ethane and heat which will quickly raise the pressure and temperature inside the chamber. A pressure relief valve is fitted in case maximum pressure limits are exceeded.

During permeation, the DEZ reactions with the acids and water will generate heat. The book temperature will rise. Paper begins to degrade at 100° C, and other book materials may be damaged. At 150° C, the degradation can be very rapid. Therefore, temperatures inside the chamber are kept well below 100° C. At the same time, however, it is undesirable for either the DEZ vapors or the ethane gas to condense inside the chamber. Therefore, the temperature of the internal surfaces within the chamber must be kept above both dew points.

The most critical constraint in the process is the stability of DEZ. DEZ begins to decompose at 120° C. At 150° C the decomposition will become self-sustaining and uncontrollable. Therefore, temperatures throughout the system, including the chamber, are kept below 80° C. The present system design goal is to keep book temperatures at 60° C or below. Ongoing pilot plant tests will confirm whether this goal is feasible.

Rehydration also generates heat, about as much and as rapidly as does permeation.

Temperature control in various pieces of hardware is maintained by circulating heated or cooled oil. The book temperature is controlled by introducing heated or cooled inert gas.

Besides monitoring and/or controlling temperature, pressure, and book weight, an accurate inventory of DEZ is maintained. The total amount of DEZ at the start of the cycle must be accounted for at the end of the cycle. All DEZ holding vessels are weighed. The difference in weight before and after treatment must be balanced by the amount of DEZ that was reacted in the books. The latter amount can be determined by the weight gain in the books during permeation. Pilot plant tests will confirm whether this measurement or some other means of monitoring is feasible. The importance of maintaining an accurate DEZ inventory will be evident in the discussion of the first pilot plant's accident, in chapter 5.

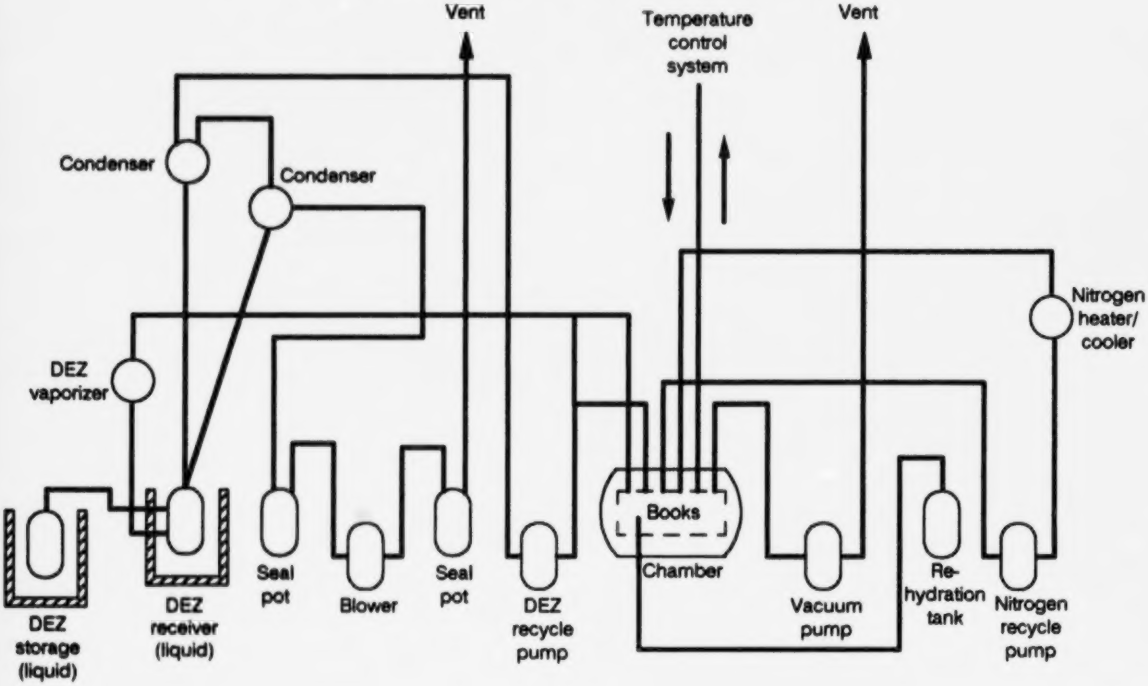
In general, the process is relatively straightforward, but it does involve a complex sequence of operations. It also requires extensive monitoring to ensure safe and efficient operation. A computerized distributive control system (DCS) has been incorporated to assist the operator in monitoring, managing, and controlling the system.

The computer continuously monitors pressures, temperatures, flow rates, etc. throughout the system. In addition, it continuously monitors the status of all valves (e.g., open/closed) and pieces of equipment (e.g., on/off). Before the initiation of any action, the computer checks these parameters against a set of predetermined values, called "permissives," that are programmed for that stage of the process. Any action, whether initiated by the operator or the computer, cannot be performed if these permissives are not satisfied. If the permissives are breached during operation, or in the case of an emergency, the computer is programmed to safely halt or shut down the process. The interaction between the human operator and the computer is critical for the safe operation of the plant and will be discussed further in chapter 5.

Cycle Times

Current estimates of the cycle time for a full-scale operation range from 45 to 55 hours. The cycle time is limited mainly by the rate at which books can be dehydrated. Depending on how the books are stacked in the chamber, the larger the number of books being treated, the longer it takes for books in the interior of the stack to give up their water. Dehydration times can be affected by the rate the water vapor is pumped out of the chamber. Pumping too fast, however, will lower the book temperature too fast. As of this writing, estimated dehydration times for a full-scale operation would range from 25 to 30 hours. Permeation, in a full-scale operation, would take from 6 to 9 hours and rehydration 7 to 8 hours. Other steps as well as loading and unloading books would bring total cycle time to 45 to 55 hours.

Figure 6.—Simplified DEZ Process Flow Diagram


Vent
Temperature control system
Vent
Condenser
Condenser
Nitrogen heater/ cooler
DEZ vaporizer
Books
Chamber
DEZ storage (liquid)
DEZ receiver (liquid)
Seal pot
Blower
Seal pot
DEZ recycle pump
Vacuum pump
Re-hydration tank
Nitrogen recycle pump

SOURCE: Office of Technology Assessment, 1988

Hardware

The hardware and capital investment required for the Library plant is large. Because of the hazardous nature of DEZ, the need to locate in an area zoned for chemical operations, and the lack of available space near the Library of Congress, a separate facility away from the Library would have to be built. A simplified flow diagram is shown in figure 6. The system would consist of the following subsystems:

- a processing chamber or chambers;
- a vacuum system;
- a DEZ handling system that would nominally include liquid DEZ containers, a DEZ vaporizer, condenser(s), pump, and sealpots;
- a nitrogen gas system;
- a water vapor system; and
- a heat exchanger system used for temperature control.

As mentioned, the operation of the system will be managed by a computerized distributive control system.

Capital costs are discussed more fully in chapter 4. A detailed design of the full-scale plant has not yet been started but the general approach would be to scale-up from the pilot plant making any modifications that appear warranted after completing pilot plant tests. The book treatment capacity of the pilot plant is about 1/25th the scale envisaged for the full-scale plant.

DEVELOPMENT HISTORY OF THE DEZ PROCESS

Objectives

Since its beginning in 1973 the objective of the mass deacidification development program has been to develop a process that would:

- process large numbers of books and other formats, capable of treating the entire book collection in 20 years;
- require no preselection (i.e., be compatible with all other book materials, inks, pigments, etc. and cause no visual or tangible differences in the treated material);
- prolong the life of the book as much as possible (i.e., permanently and completely neutralize all acids and deposit a sufficient permanent and uniform alkaline buffer);
- be cost-effective; and
- be safe.

Selection of DEZ

Based on the above goals, the Library decided to pursue the development of a vapor phase process as opposed to a liquid phase process. The Library's chemists felt that large numbers of books could be more quickly and uniformly treated by vapor reactants diffusing around and through the books. Also, the liquid phase processes in use required pretesting to ensure that the materials to be treated were compatible with the solvents used.

There were a few vapor phase deacidification processes that had already been developed. A morpholine process was developed at the Barrows Laboratory, and two amine-based processes, one using cyclohexylamine carbonate and one using ammonia, were developed in England and India, respectively.

The Library experimented with the morpholine process. The principal limitation of this process is its bad odors that cause headaches and nausea in process workers. Other problems include an insufficient buffer, and questionable health effects. The process had the potential of forming nitrosamines which could be inhaled by workers. Morpholine can also discolor paper.

The cyclohexylamine carbonate process was developed by Langwell in the early 1960s. The patents now reside with B.G. Robertson Laboratories, London. Interleaf, Inc. is the sole distributor of the product in the United States. This is basically a manual process, but is so simple that it could be used to treat a substantial number of books. Cyclohexylamine carbonate crystals are placed in a packet in a book every 100 pages. Cyclohexylamine is volatile and vapors containing the carbonate compound permeate through the book, reacting with and neutralizing the acids. This process does not leave an alkaline buffer, however, and the byproducts from the acid reactions are themselves volatile. Under certain conditions, these byproducts can revert back to the acid and give off an ammonia-like odor. Also, at the time the Library was investigating these various processes, the health effects of cyclamates were a concern, raising questions about the health effects of cyclohexylamines as well.

Kathpalia, also in the 1960s, developed an ammonia process. It suffers from many of the same problems as the cyclohexylamine process, except that the acid reaction byproducts are even more volatile.

Unable to justify developing any of the existing processes or chemicals, the Library began to search for its own chemical and process. Table 2 is a list of the compounds that were evaluated. To meet their objectives, the chemical had to have a high vapor pressure within the temperature limits of the process (i.e., between 0 and 80° C), it had to react with all acids present in books, without forming any deleterious reactions with any of the other book materials, the acid reaction byproducts had to be stable, and an alkaline buffer had to be created to neutralize any acids that could form after treatment.

Metal alkyls represented a class of compounds that met these various requirements. Metal alkyls are very reactive and will quickly neutralize all the types of acids found in paper. In addition, either directly or indirectly, the metal alkyls react with moisture in the paper to form stable alkaline com-

Table 2.—Compounds Tested by the Library's Laboratory for Deacidification of Paper, 1970-74

1. Triethyl aluminum
2. Diethylzinc
3. Ethylene imine cyclohexyl amine carbonate
4. Morpholine
5. Hexamethylene diamine formaldehyde
6. Calcium hydroxide and calcium bicarbonate (Barrow two step)
7. Calcium chloride and ammonium carbonate (double decomposition)
8. Borax
9. Methyl zinc carbonate
10. Magnesium acetonyl acetonate
11. Magnesium hexafluoroacetyl acetonate
12. Barium acetyl acetonate
13. Cyclohexyl amine carbonate (Langwell VPD)[a]
14. Silane deacidification agent (Dow Corning Z-6020)
15. Sodium carbonate and magnesium chloride
16. Magnesium methoxide and methyl magnesium carbonate[b]
17. Zinc ammonium carbonate
18. Ammonium zirconyl carbonate

[a] Compound used in the Interleaf process.
[b] Compound used in the Wei T'o process.

SOURCE: Library of Congress.

pounds. The amount of stable alkaline compound deposited depends on the amount of moisture in the paper and can, therefore, be controlled.

The metal alkyls, however, were of concern regarding one major objective of the development program—safety. Metal alkyls are pyrophoric. If allowed to come in contact with air, they will spontaneously ignite. Furthermore, they react very vigorously with water. Both reactions give off ethane which is flammable and potentially explosive under certain conditions. The metal alkyl-water reaction that would deposit an alkaline buffer in a book involves very small volumes of these reactants and therefore is not a violent reaction. However, it will generate heat and must be controlled.

Metal alkyls have been used for many years in a variety of applications. Their major use today is as an intermediate in the manufacturing of polyethylene and polypropylene. Fully aware of the hazards associated with metal alkyls, the Library felt that these hazards were manageable and that the advantages of the compounds were worth the costs associated with developing a safe process.

Of the various metal alkyls tested, DEZ had the highest vapor pressure in the temperature range involved. Initial tests indicated that papers exposed to DEZ vapors were deacidified, had an alkaline zinc oxide buffer deposited, and appeared not to be adversely affected in any way. Based on these conclusions, the Library proceeded to develop a process around DEZ.

Process Chemistry

In the early stages of developing the DEZ process, the following reactions were thought to occur:

- DEZ vapors react with both weak and strong acids to form stable zinc salts and ethane gas.
- DEZ vapors react with hydroxyl groups on the cellulose molecule to form an unstable compound, ethylzincoxycellulose. During rehydration, this unstable compound would form zinc oxide and ethane and return the cellulose to its original form.
- DEZ vapors react with aldehyde groups on the cellulose molecule to form a stable alcohol and ethane gas.

Originally, processing was based on eliminating as much of the water as possible, and using the hydroxyl reaction to form the alkaline buffer. It was hypothesized that the amount of water in a book, nominally 6 percent of the book's weight, would impede the permeation of DEZ into the center of the book by immediately reacting with the DEZ on the book's outer edges. It was also thought that partial dehydration of the books during permeation would leave a moisture gradient within the books that would result in an undesirable gradient in the amount of zinc oxide that would get deposited. The hydroxyl group, however, could be expected to remain evenly distributed throughout the paper and the books and result in a uniform distribution of zinc oxide buffer.

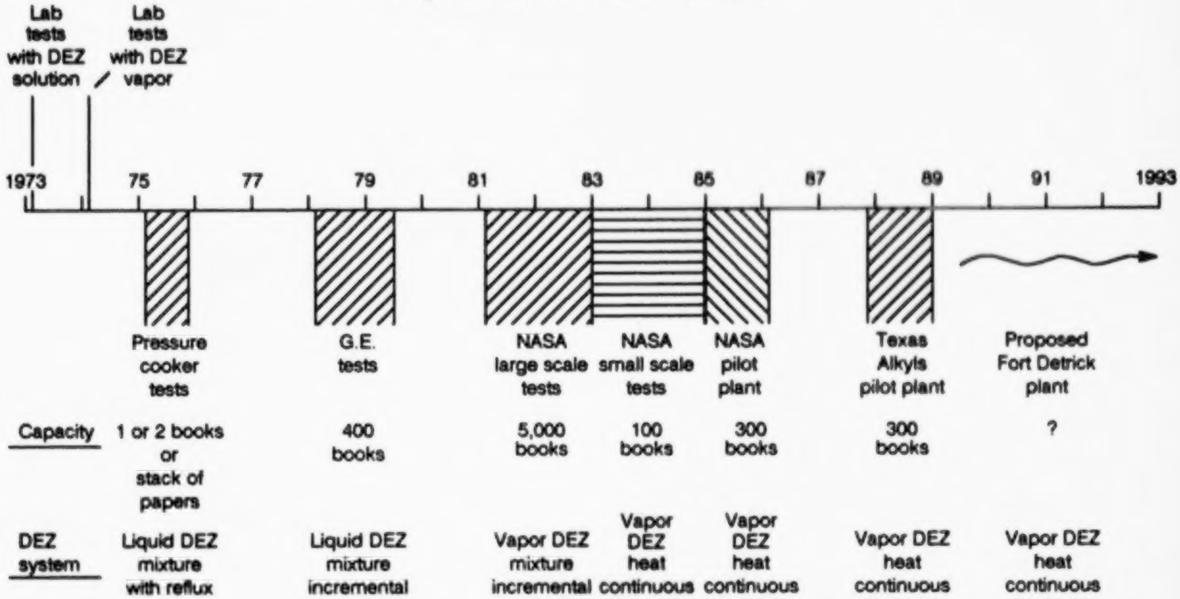
Later experience indicated that this hydroxyl reaction must be slow and that most of the alkaline buffer that gets deposited is the result of the water reaction. A test that exposed very dry pure cellulose paper to DEZ vapors supports this observation. Therefore, the amount of alkaline buffer deposited in the books depends to a large extent on the amount of water left in the book. It also depends on the amount of DEZ the books are exposed to, possibly the rate and time of exposure, and the particular properties (e.g., permeability) of the paper being treated.

After development had proceeded, the Library chemists became aware of studies that indicated zinc oxide could promote photodegradation of paper. The Library conducted a few tests that showed treated papers were more sensitive to photodegradation.[1] Although photodegradation is not considered a serious problem at the Library, especially in relation to acid deterioration and other degradation mechanisms, a solution to the problem was sought. The solution sought by the Library was to convert zinc oxide to zinc carbonate, which does not promote photodegradation, by soaking the books in carbon dioxide after rehydration. However, subsequent tests have shown that little if any zinc carbonate forms after soaking the books in carbon dioxide. Whether the carbon dioxide soak is useful and will remain as part of the treatment will be determined in future tests.

Development History

The evolution of the DEZ process is shown in figure 7. The Library began bench-scale development in 1974. During these bench-scale tests, a pressure cooker was used as a process chamber. Sheets of test paper (or segments of books) were placed in the cooker. Air was removed and the books dehydrated. Dehydration continued until the pressure in the cooker stabilized with the vacuum pump turned off, indicating maximum dehydration. DEZ mixed in various concentrations with hydrocarbons (e.g., octane) was injected into the cooker as a liquid. The liquid sat at the bottom of the chamber and evaporated. Vapors permeated up through the paper of books, deacidifying the paper. Unreacted vapors were condensed at the top of the cooker and the liquid recycled. Rehydration was typically accomplished with nitrogen gas or alcohol saturated with water vapor which also neutralized any unreacted DEZ liquid remaining at the bottom of the cooker.

Figure 7.—Evolution of DEZ Process



	Pressure cooker tests	G.E. tests	NASA large scale tests	NASA small scale tests	NASA pilot plant	Texas Alkyls pilot plant	Proposed Fort Detrick plant
Capacity	1 or 2 books or stack of papers	400 books	5,000 books	100 books	300 books	300 books	?
DEZ system	Liquid DEZ mixture with reflux	Liquid DEZ mixture incremental feed, no reflux	Vapor DEZ mixture incremental feed with recovery	Vapor DEZ heat continuous feed with recovery	Vapor DEZ heat continuous feed with recycle	Vapor DEZ heat continuous feed with recycle	Vapor DEZ heat continuous feed with recycle
Cycle times	~ 10 hrs	24-72 hrs	244 hrs	~ 45 hrs	?	Est. 50-90 hrs	?

SOURCE: Office of Technology Assessment, 1988

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[1] George B. Kelly and John C. Williams, "Inhibition of Light Sensitivity of Papers Treated With Diethylzinc," presented at the Annual Meeting of the American Chemical Society, Washington, DC, September 1979.

Photo credit: Library of Congress

Original pressure cooker test of DEZ at Library of Congress

Typical dehydration times were about 5 hours. Permeation times were about 5 hours.

The treated papers were evaluated for pH, zinc oxide content, and brightness. Some of the papers' fold endurances were also measured after accelerated aging. Typically, the results were positive, and are discussed in more detail in the next chapter.

The goal of the program, to treat the entire book collection in 20 years, required that the system had to treat about 1 million books per year. If two single chambers were used, 7,500 books would have to be treated in a single chamber. To test the feasibility of the process at this scale, a series of larger scale tests were begun.

In 1979, the Library contracted with General Electric's (G.E.) Valley Forge Space Center to use one of their large thermal/vacuum chambers, normally used for simulating space environments. The tests treated 400 books at a time. The principal objective of these tests was to confirm the feasibility of the process at this moderate scale. In addition, a variety of processing conditions were evaluated, including different ways of stacking the books in the chamber.

The G.E. chamber that was used was 12 feet in diameter and 26 feet long. Various processing hardware was fitted onto the chamber. The system was essentially the same as that used in the Library. A vacuum pump removed the air from the chamber. Liquid DEZ mixed with a hydrocarbon, Isopar E, was introduced into the chamber and allowed to vaporize in the chamber (the last test used 100 percent DEZ, called neat DEZ). However, because of the larger volumes of DEZ required to treat 400 books, it was introduced incrementally, as a precaution, to ensure that the amount of heat generated would not raise the temperature above the limits mentioned earlier. A separate pump was used to remove the ethane and unreacted DEZ vapors. These were removed into sample bottles. Unreacted DEZ liquid at the bottom of the chamber was neutralized with alcohol.

A total of four tests were conducted. Complete deacidification was achieved in two of the tests. Zinc oxide contents ranged from 0.5 to 1.4 percent. It was concluded that the best operating conditions were long exposures at low pressures using 100 percent DEZ.

The best book-stacking configuration seemed to be closed with the spine down. However, in each of the tests, tide marks were observed on the covers. The tide marks were diffraction patterns caused by excess zinc oxide. It was hypothesized that the tide marks were caused by a thin film of DEZ trapped between the books. Book covers generally hold more water than the inside pages, providing excess moisture for the excess DEZ to react with. It was recommended that books be separated to allow good circulation of DEZ between the books.

Another observation was that moisture and small air leaks into the system seemed to produce unwanted zinc oxide throughout the system, presenting a potential maintenance problem. It is also possible that small air leaks lead to the visible zinc oxide surface deposition on books.

The test also demonstrated that relatively large amounts of DEZ could be handled safely during treatment. Further work would have to be done to optimize the treatment, to reduce the amount of cycle time, and to remove the tide marks from the covers.

Encouraged by these results, the Library continued scaling up the process. In 1981, the Library contracted with NASA's Goddard Space Flight Center to use one of their thermal/vacuum chambers to treat 5,000 books.

Photo credit: Library of Congress

Chamber used at NASA-Goddard for DEZ treatment

The size of the Goddard chamber was 10 feet in diameter and 15 feet long. The system was basically the same as the one used at G.E. with one major exception. DEZ, mixed with mineral oil, was first fed into a vaporizer and introduced into the chamber as a vapor. It was fed incrementally as a precaution and to control temperature rises in the books. The only temperature control for the books was radiant heat from the chamber walls. The unreacted DEZ was condensed and recovered. Alcohol was still available should any liquid DEZ be left in the chamber after permeation. Saturated carbon dioxide was introduced during rehydration to test the conversion of zinc oxide to zinc carbonate.

In addition to the system instrumentation, individual books were also monitored for weight and temperature to better track the process throughout the stack of 5,000 books.

Although this was basically a feasibility test, a substantial amount of engineering was done on the various pieces of hardware. A large number of safety reviews were conducted including a typical NASA fault tree analysis. Also, 15 separate subsystem operating procedures were detailed. This single test, including planning, design, and construction, took 1 year.

Books were loaded in crates, separated by spacers, and marked by their location within the chamber. Dehydration took 4 days (96 hours). The books were exposed to DEZ incrementally for 6 days (124 hours). The books were rehydrated for 24 hours.

The results of the test were mixed. There were three major problems.

First, treatment was not uniform throughout the stack of books. Books at the bottom half of the chamber were completely deacidified and had a average zinc oxide content of 2.2 percent. Books at the top levels of the chamber were hardly deacidified at all and had almost no zinc oxide deposited. Books in the middle of the stack were partially deacidified; the outer portion of pages were deacidified, but at the center of the book the pages were not deacidified. These middle books also had very little zinc oxide (about 0.2 percent). These results agreed with the data collected from the individual books that were monitored during the process.

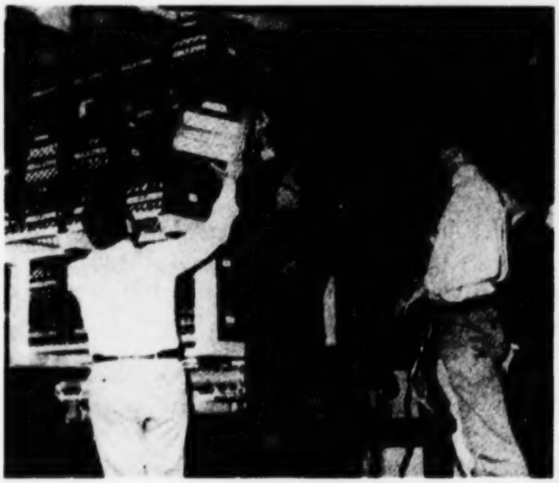

Photo credit: Library of Congress

Books being prepared for NASA-Goddard test of DEZ treatment

Books at the top showed little temperature rise. The temperature of books in the middle rose near the end of the process, and the books at the bottom showed early increases in temperature. The evolution of ethane also indicated that most of the reactions occurred early in the process.

The cause of this first problem was judged to be stratification of the DEZ vapors and the evolved ethane. DEZ was introduced near the bottom of the chamber. Ethane, being lighter, naturally rose and sat at the top of the chamber. With only small amounts of DEZ being injected at any one time, the environment inside the chamber was basically static. Ethane impeded the flow of DEZ vapors to the upper books.

The second problem was that the zinc oxide was deposited in rings. The concentration of zinc oxide in these rings was high on the outside rings and diminished towards the center of the page. The rings were blamed on the incremental pulsing of the DEZ into the chamber. The hypothesis was that as the permeation step proceeded, water continued to migrate out to the edges of the books. With each new pulse, more zinc oxide would be deposited on the outside edges.

The third problem was that tide marks remained on the covers, duplicating the patterns of the spacers used to separate the books in the crates.

However, the tests were conducted safely at this scale.

To solve the treatment problems the Library continued with a series of smaller scale tests at Goddard. A large diffusion pump housing was used as the process chamber. Books were stacked in the test chamber in two 50-book stacks.

Thirteen tests were conducted. The first test duplicated the conditions and, thus, the problems of the 5,000-book run. The rest of the tests were aimed at solving the various problems. To correct the ring problem, a continuous DEZ vapor feed (1 pound per hour (lb/hr)) and collection system was developed. To correct for the stratification in the chamber, DEZ gas was fed through the system at a high rate to induce better mixing in the chamber. A variety of spacer designs and spacing dimensions were also tested.

Cycle times of these small-scale tests were reduced to about 45 hours. Complete deacidification throughout the stack of books was achieved in a number of these tests. Uniform zinc oxide was also achieved. None of the spacer designs totally eliminated the tide marks. However, by minimizing the contact between book and spacer the excess deposition of zinc oxide was reduced almost beyond detection.

Encouraged by the results of these small-scale tests, the Library decided to build a pilot plant at Goddard. This would be the first attempt at engineering a system for commercial feasibility. Northrup, NASA's engineering contractor at Goddard who designed and operated the 5,000-book and the small-scale tests, was responsible for the design, construction, and operation of the pilot plant. The plant was built in an existing NASA building.

The system was designed to treat 300 books. Two new continuous DEZ vaporizers were to be tested. One would feed DEZ vapors into the chamber at 60 lb/hr, the other would feed it in at 200 lb/hr. The DEZ vapors were to be condensed and recycled during the process.

Construction was completed in October 1985. In December, during the final check of the system, however, an accident occurred. A fire broke out in the chamber. There were no injuries; property damage to the building was minimal but somewhat more extensive to the processing equipment. While attempting to safely deactivate the system, an explosion occurred and another fire broke out. Again there were no injuries, however, the system was judged by NASA officials to be unsafe and an Army demolition team was brought in to safely decommission the plant with small explosives.

A more detailed account of the incident will be given in chapter 5. The information for this OTA study was taken from the NASA Accident Investigation Report of September 4, 1986, as well as OTA and NASA meetings and conversations during August-September 1987. However, the principal finding of the in-house accident review committee was that standard safety procedures and practices were not followed in both the design and operation of the the plant. The care and detailed analysis that went into the test facilities were not repeated in the pilot plant.

After the accident, the Library of Congress discontinued its working arrangement with NASA. However, using the experience gained in the failure of the first pilot plant, and implementing all of the recommendations made by the NASA accident review team, the Library has contracted for and built a second pilot plant at Texas Alkyls' site outside Houston, Texas. Texas Alkyls has been the Library's principal supplier of DEZ and has over 20 years of experience in manufacturing and handling DEZ and other metal alkyls.

The plant has been designed to treat about 300 books. The chamber is 6 feet in diameter and 6 feet long. The process uses 100 percent DEZ. The DEZ is continuously vaporized and introduced into the chamber at high flow rates. Unused DEZ gas and ethane is continuously pumped out of the chamber with the unused DEZ vapor condensed and recycled and the ethane vented.

DISCUSSION

A number of tests have been planned for the new pilot plant. In general these tests will provide engineering and operational information for the commercial plant, including maintenance needs, manpower requirements, reliability and safety of the design and operations, and optimal temperature/pressure parameters for the various steps in the process. Specifically, there are also four major development issues that still need to be resolved. These are optimizing the DEZ flow rate, optimizing book configuration, reducing cycle time, and collecting scale-up engineering data.

The flow rate of DEZ into the chamber is very critical for two reasons. First, it is important to simultaneously expose as many books as possible to the DEZ vapor. DEZ will start to react quickly with the first books that it comes in contact with. Therefore, if the DEZ is not uniformly distributed at a high enough rate, deacidification will not occur in a reasonable exposure time.

The flow rate is also critical in ensuring that the DEZ and the ethane that is evolved during permeation will be thoroughly mixed, prohibiting a stratification of gases within the chamber.

The small-scale tests run at NASA after the 5,000-book run showed that a high DEZ flow rate can eliminate the problem. A principal task during the pilot plant tests will be to duplicate these results. The pilot facility is capable of generating flow rates that would be equivalent to 10,000 lb/hr in the full-scale plant, but it is doubtful that a flow rate this high will be necessary.

Book configuration also plays a role in the circulation of vapors within the chamber. The principal issue involving book configuration, however, is the spacing between books. Spacing between books plays a critical role in preventing the excess zinc oxide coating from depositing on book covers. The problems of ring formation, chamber uniformity, and cover staining were resolved in the final small-scale tests at Goddard. The pilot facility will be used to duplicate these results.

The question of cycle times was discussed in the process description. A conservative estimate of the total treatment time ranges from 55 to 72 hours. A goal of the pilot plant studies is to reduce this, if possible, to 48 hours. This would greatly increase the number of books that could be processed and lower the costs.

The rate-limiting step appears to be the dehydration step. The time it takes for water to diffuse out of the books will depend on the rate at which the chamber can be pumped to a rough vacuum, and the rate at which the book's temperature can be controlled. The chamber vacuum pump is sized to bring the chamber down to a rough vacuum (about 2.5 torr[2]) in 12 hours. However, pumping too fast may lower the book temperature too much. A warm nitrogen gas step would then be required to raise the temperature of the books back to a higher temperature. Book configuration may also affect the time needed for this cycle. Book carts and spacers must be designed to allow books in the interior of a stack enough time to get to the desired moisture content.

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[2] A measure of absolute pressure in millimeters of mercury—1 torr is equivalent to 1/760 of atmospheric pressure.

The principal issue in scaling up to a commercial plant is whether to achieve the desired capacity with one larger chamber (up to 7,500 books per run) or to design multiple chambers of a size close to that of the pilot plant chamber. There are many reasons that favor the latter approach.

Multiple chambers would basically reduce the amount of down time in the system. If one chamber is shut down, the others can continue to operate. It also allows the various subsystems—i.e., the DEZ recycling pump, the chamber vacuum pump, etc.—to operate more continuously reducing the chance of failures associated with the startup and shutdown of those components.

Also, keeping the chamber not much larger than the pilot plant chamber will introduce less uncertainty in reproducing the flow characteristics achieved in the pilot plant. Although most of the scaling up associated with a (large) single-chamber design would be relatively straight forward, reproducing the flow characteristics in a greatly enlarged chamber would not.

The principal disadvantages in going to a multiple-chamber design would be some increase in the complexity of operations. Cost factors would also need to be evaluated. Depending on their design, several multiple chambers may cost more or less than a single large one. Also, the chemical plant section for multiple chambers could possibly be smaller and lower cost. Finally, with multiple chambers, the control of the process would require careful monitoring by the distributive control system and greater complexity in the interlock design and operations which may also affect cost.

Chapter 3

Effectiveness of the DEZ Process

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Chapter 3

Effectiveness of the DEZ Process

INTRODUCTION

The purpose of this chapter is to assess the effectiveness of the DEZ process and the expected benefits of the Library's program. The Library of Congress has performed a substantial number of tests during the development of its process and has made the results available for this study. Over the past several years, however, the Library had not widely disseminated this test data or published the results. Upon the request of OTA, the Library has written a report of its small-scale test program at NASA. This is separately available from OTA or the Library upon request.[1] This, together with data from the original patent, G.E. and NASA contractor reports, and interviews with the Library form the basis of this chapter.

This chapter is divided into four major sections: 1) *Goals and Criteria* describes the objectives of the Library's deacidification program; 2) *Library of Congress Test Methods* describes procedures used by the Library to evaluate DEZ treatment; 3) *Library of Congress Test Results*; and 4) *Discussion* presents OTA conclusions about the effectiveness of the DEZ process.

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[1] Library of Congress, Preservation Research and Testing Office Report on the Thirteen Small-Scale Test Runs of the DEZ Deacidification Process at Goddard Space Flight Center in 1983, 1984, 1985; December 1987, unpublished.

GOALS AND CRITERIA

The goals of the Library's process development program relating to effectiveness are:

- prolong the life of paper in books and other formats as long as possible,
- no preselection, and
- capable of treating the entire book collection in 20 years.

In order to achieve these goals, the Library has articulated a set of criteria that the process must satisfy:

- a demonstrated improvement in book life,
- a complete and permanent neutralization of all acids,
- an adequate and permanent deposition of an alkaline buffer,
- uniform treatment within each book and throughout all books,
- compatibility with all other book materials,
- capable of treating about 1 million books per year, and
- capable of treating other formats, e.g., boxed manuscripts, maps.

The life of a book can be defined as the time it takes for a book to deteriorate to a point where its information is no longer available. There are no standards, however, by which to measure deterioration or at what point it has rendered the information in a book inaccessible. A commonly used measure of book life and the one used by the Library is the decline in fold endurance. Fold endurance is the number of times a piece of paper can be folded, either 90 or 270°, under tension, before it breaks. The fold endurance of paper will decrease with age and is indirectly related to the degree to which the paper has degraded. The Library compares the decline in fold endurance of treated and untreated paper to demonstrate the effectiveness of its process. The results of fold endurance tests are influenced by depolymerization of the cellulose molecule, and by changes in the degree of crystallization and crosslinking—all chemical changes which are mainly responsible for the degradation of paper upon aging. The Library uses this test because they have concluded that it is more sensitive than other commonly measured physical properties, such as tensile strength, resistance to tear, wet strength, or burst.

The decline in fold endurance must be measured over time. Because the life of modern papers may range from 50 to 100 years, natural aging is not practical for analysis. Therefore, treated and untreated papers must be aged artificially. Artificial, or accelerated, aging is done in an oven under controlled temperature and humidity. The assumption is that the mechanisms responsible for natural aging can be accelerated if the paper is exposed to elevated temperatures. A rough correlation is that 72 hours at 100° C is equivalent to 25 years of natural aging. The actual relationship will vary from paper to paper and must be determined by taking measurements at at least two different aging temperatures. It may also depend on the initial age of the paper.

To prolong the life of the books as much as possible, the Library maintains that the process must completely and permanently deacidify all of the acids present in the paper. Stable papers have a pH of at least 7. The Library has set a pH of 7 as the minimum for adequate deacidification. If the pH of paper gets too high it actually becomes too alkaline and can begin to deteriorate by other mechanisms.

The deacidification must also be permanent so that the treated book does not become untreated, i.e., so that part or all of the byproducts formed during deacidification do not spontaneously react and revert back to acids over time. As mentioned earlier, the Library ruled out the amine-based processes for this (and other) reasons.

In addition, the process must deposit a sufficient amount of permanent alkaline buffer throughout the book. A treated book can become acidic again due to the continued conversion of alum, lignin, and other book materials to acids, or from the absorption of pollutants from the environment. A permanent alkaline buffer will protect against this reacidification. Again, the alkaline buffer must be permanent and not decompose or migrate out of the paper, to provide maximum protection.

An adequate amount of buffer is required to provide the protection over a long period of time. Originally the Library considered a goal of 2 to 3 percent zinc oxide. The Library has since determined that for the DEZ process, depositing 1.5 to 2.0 percent by weight of zinc oxide in the paper will provide the best enhancement of permanence at the lowest cost (see figure 8).

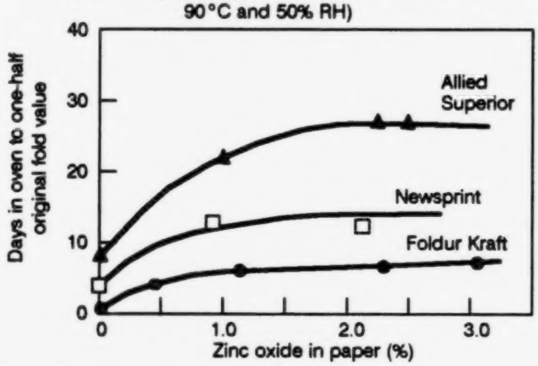
Of course, uniform treatment is necessary to ensure that the entire book is protected. Areas that are not treated, or acids that are not neutralized, will continue to degrade. For books, it is imperative that the treatment reaches into the spine of the book.

Compatibility with other materials found in books, such as adhesives, labels, covers, inks, pigments, coatings, etc., causing no visual or tangible differences in the treated paper means that no preselection or sorting would be necessary prior to treatment. To some extent compatibility is an aesthetic issue, but one that is insisted on by most librarians and curators. However, there are practical reasons as well. For example, if inks or colors run or transfer, or if labels fall off, information may be lost.

The Library has set for itself the goal of treating all of its book collections within a 20-year period. This means that between 1 and 1.5 million books must be treated each year. The Library also intends for the process to have the ability to easily and effectively treat other formats because all paper collections have similar acid embrittlement problems.

Figure 8.—MIT Fold Test $t_{1/2}$ v. Zinc Oxide Content

(three test papers aged at humid conditions — 90°C and 50% RH)



SOURCE: Library of Congress

LIBRARY OF CONGRESS TEST METHODS

The Library uses a variety of standardized tests described below to evaluate the effectiveness of their process.

To demonstrate the effectiveness of the DEZ process in extending the life of a book, treated and untreated papers are artificially aged in an oven at 90° C and a relative humidity, RH, of 50 percent and a dry oven at 100° C and 0 percent RH. Aging takes place for up to 100 hours with samples pulled at 5- to 10-hour intervals. Following aging, specimens taken from both the treated and untreated paper are then tested in an M.I.T. fold endurance machine. (TAPPI Standard T 511 su-69, "Folding Endurance of Paper.") The machine repeatedly bends the paper specimen through a 270° angle, with 0.5 kg of tension (a modification of the TAPPI standard) on the paper. The number of times the paper is bent before it breaks is recorded, and represents the fold endurance. By comparing the difference in the loss of fold endurance, after similar accelerated aging times and conditions, the difference in the rate of deterioration between the treated and untreated paper can be determined. Alternatively, comparing the number of days (i.e., years) it takes before the paper has lost all of its fold endurance can provide a measure of how long the life of the book has been prolonged. This measurement is usually performed on test papers—not papers from actual books. Some researchers outside the Library have noted that fold endurance is sensitive but over a relatively narrow range in comparison to tensile or certain other measurements and that fold endurance works best for new, relatively strong papers.

To determine whether deacidification has been complete, the Library determines the average pH of the paper using a modified standard TAPPI test.[2] Randomly selected pages from a randomly selected book, are ground up into a slurry and the pH of the slurry measured by titration. This does not give an indication of the uniformity of treatment across the page, but is a more sensitive measurement of pH. Specific pH values mentioned in this chapter are the results of slurry tests.

To ensure that enough zinc oxide has been deposited, the Library randomly selects a page or a portion of a page from a randomly selected book, macerates the paper into a slurry and determines the amount of zinc oxide present by acid titration.

Nonquantitative tests are used to demonstrate completeness of treatment. The Library determines whether deacidification has been complete by spraying randomly selected pages from randomly selected books or paper with a pH-indicating solution. If the paper has been completely neutralized, the entire page, including down into the spine of the book, will be a color associated with a pH of 7 or greater.

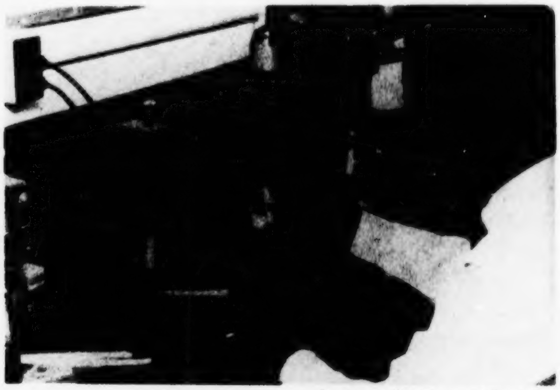


Photo credit: Library of Congress

Fold endurance test apparatus

Photo credit: Library of Congress

pH test apparatus

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[2] TAPPI Standard T 509 os-77; "Hydrogen Ion Concentration (pH) of Paper Extracts—Cold Extraction Method"; the Library modification is to use a blender to produce a slurry.

If the treatment has not been complete, areas on the page will be a color associated with a pH less than 7.

To ensure that the deposition has been uniform, the selected pages are placed under an ultraviolet light. The zinc oxide will fluoresce, revealing its location on the page. These visual observations have been confirmed by more elaborate quantitative measurements of uniformity across a page using x-ray fluorescence and atomic adsorption techniques. Additional evaluations of uniformity of zinc oxide deposition have been made using scanning electron microscope techniques. The microscope scans sections of the paper with electrons. When hit by the electrons, the different elements in and on the paper, will emit their own characteristic x rays. By just sensing the x rays characteristic of zinc, the location of zinc can be determined. The intensity of the x rays also gives a semi-quantitative measurement of how much zinc is present.

Visual inspection has been the principal method used by the Library to determine whether the treatment has been compatible with all other book materials. Pages of books were inspected for yellowing or other discoloration, transfer of colors from one page to another, running of inks, the accumulation of reaction byproducts, etc. The books were also inspected for any loss of adherence in areas where glues or other adhesives are used.

The Library at times has measured the brightness before and after treatment, as well. Brightness is determined by measuring the paper's blue reflectance. The paper is lit with white light from a standard lamp. The light reflecting off the paper passes through a blue filter and its intensity recorded by a photo cell. The output of the photo cell is calibrated with a standard of known reflectance.

The Library has also conducted a test to determine whether any reactions occur between the DEZ and a few of the most common materials to be found in or on books. This is discussed further in the following section.

Because of its priority to deacidify books, thus far, the Library has only conducted a limited number of tests on other formats. Zinc oxide contents and pH were measured on maps treated in the G.E. tests. The Library plans more thorough testing of other formats in 1988 at the Texas Alkyls pilot plant.

LIBRARY OF CONGRESS TEST RESULTS

Published documentation of the DEZ process' effectiveness is limited. Many tests have been run, and much data has been accumulated. However, the external reporting of the results has been limited in the view of some other preservation scientists. The principal documentation of the process' effectiveness is found in the process patent which contains the results from a collection of early lab tests and in the list of publications in appendix E. These results, and some selected data from the larger scale tests, have convinced the Library that if they can achieve a uniform deacidfication and a uniform deposition of 1.5 percent zinc oxide in the books, the life of the books can be extended between three to five times. All subsequent work has been devoted to achieving these results in scaled-up systems. Most of the data that have been collected have been pH measurements, zinc oxide content, and some fold endurance measurements. Since most of the development has involved optimizing the process, these data include good and bad results. Since the Library has not published a comprehensive report on the results of all past experiments, OTA requested the Library to prepare a report on the most recent set of tests conducted at NASA in 1985-86. That report is available separately from the Library.

Acid Neutralization

The effectiveness with which DEZ neutralizes acids is fairly well-established. DEZ is known to be an avid scavenger of hydrogen ions and therefore should react directly with all acids very quickly. Test results support this. In data presented in the patent, single sheets of various types of papers were treated for 1 hour. The results, shown in table 3, indicate that DEZ can quickly neutralize the pH of a wide variety of acidic papers, including news-

Table 3.—Comparison of pH Before and After DEZ Treatment and Zinc Oxide After DEZ Treatment for Various Papers

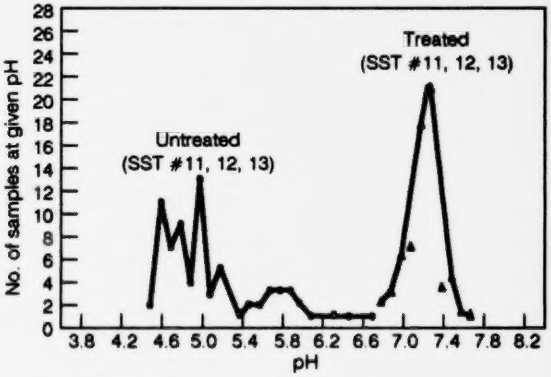
Paper	pH before treatment	pH after treatment	% zinc oxide in paper after treatment
Newsprint	5.4	7.8	0.89
Offset paper (LCIB)	5.8	7.9	2.02
Made Rite offset	5.6	8.2	1.48
Whatman filter paper #1	6.6	8.1	0.94
100% rag ledger (GPO#773)	6.2	8.0	1.37
Old book paper (rag) published 1820	5.3	8.1	0.79
Berestoke text (handmade)	4.7	7.6	1.42
Crane's distaff linen antique laid	5.2	7.7	0.54
Mead bond	5.9	7.7	0.82

NOTE: These data were taken from Patent #4,051,276 (Sept. 26, 1977). Papers were treated for 1 hour (probably individually) during Library lab tests prior to 1977.

SOURCE: Library of Congress.

print. In one case it raised the pH from a low 4.7 to a slightly alkaline 7.6. In another experiment, 32 sheets (16 sheets of bond and 16 sheets of newsprint) were stacked inside the pressure cooker and treated. pH measurements of the top, middle, and bottom sheets showed that DEZ could effectively penetrate and neutralize acids (see table 4). In another experiment, a book was cut in half and treated. Pages throughout the book were deacidified, the pH after treatment averaged 7.36, showing that DEZ could effectively penetrate a closed book. Figure 9, showing results of pH measurements from NASA test runs, also indicates that a variety of papers with different acid contents can be fairly uniformly brought to pH values clustered in a narrow range (±0.5) around 7.2.

Figure 9.—Typical Distribution of Slurry pH Values by Untreated and DEZ Treated Books



SOURCE: Library of Congress

The byproducts of the neutralization are zinc salts. The principal reaction is believed to be between DEZ and sulfuric acid (the major acid species in paper) to form zinc sulfate. The original sulfuric acid was formed by water reacting with the alum (aluminum sulfate). Water, too, can react with zinc sulphate, to reform acid. Some researchers have postulated that the reformation of acid from zinc sulfate could lead to a depletion of the zinc oxide buffer more rapidly than anticipated. However, the Library has investigated this and concludes that

Table 4.—pH and Zinc Oxide Content of DEZ Treated Papers for Various Locations

	Bond paper		Newsprint	
	pH	%ZnO	pH	%ZnO
Untreated	5.3	0	4.9	0
Treated:				
Sheet #1 (top of pile)	7.7	0.81		
Sheet #16 (center of pile)	7.7	0.62		
Sheet #17 (center of pile)			7.7	0.58
Sheet #32 (bottom of pile)			7.7	0.81

SOURCE: U.S. Patent #4,051,276.

the acidity contributed by zinc sulfate is much less than the buffering provided by zinc oxide. Test results from paper treated in a liquid solution of DEZ and hexane show that the pH of the treated paper can be maintained after aging, whereas the pH of the untreated paper drops dramatically (see table 5). These tests have not been performed with papers treated with DEZ vapors, nor was it stated how much zinc oxide was deposited or consumed.

Deposition of Alkaline Buffer

Patent data from early lab tests shows that a wide range of zinc oxide contents can be achieved. In the papers treated for 1 hour, zinc oxide contents ranged from 0.54 to 2.02 percent. (See table 3.) Zinc oxide contents in both the sectioned book and in the stack of papers that were treated, showed zinc oxide contents well below 1.5 percent. In the experiment that exposed a stack of papers to higher amounts of DEZ, zinc oxide contents up to 3.69 percent were achieved. Zinc oxide contents as high as 9 percent have been deposited. The Library plans to conduct more extensive tests of this type during their current pilot plant tests.

Table 5.—Drop in pH Treated v. Untreated Paper

	pH	
Paper	Before aging	After aging 12 days[a]
Offset GPO #21056:		
Untreated	6.8	4.6
Treated	7.6	7.1

[a] Aged at 90 °C and 50 percent relative humidity.

SOURCE: U.S. Patent #4,051,276.

Uniform Treatment

When treating large numbers of books, complete and uniform deacidification throughout the entire batch becomes a major issue. Tests at G.E. (400 book tests) and at NASA (one 5,000-book test and thirteen 100-book tests) confirm that all books can be completely and uniformly deacidified if enough DEZ and enough time are provided. If enough time or DEZ are not provided, or if the books are not positioned in the chamber to be exposed to DEZ, or if the DEZ does not circulate properly, some of the books will not be completely treated. Deacidification is a diffusion limited process. The outer edges of the outer pages are deacidified first. The center of the center page is deacidified last. The results of the G.E. tests are shown in table 6. In two of the tests deacidification was incomplete. The effect of poor DEZ circulation is demonstrated by complete lack of deacidification of books located near the top of the 5,000-book chamber. (See figure 10.) Complete deacidification in these tests was determined by spraying selected pages with a pH indicator solution. Average pH determinations were made by cold extraction titration. Because the results of the NASA tests were mixed, it is important that the pilot plant tests currently underway demonstrate that reasonable uniformity can be achieved under a set of standard operating conditions and with the expected variety of materials to be treated.

When uniform deacidification does occur it appears to be very uniform, regardless of book loca-

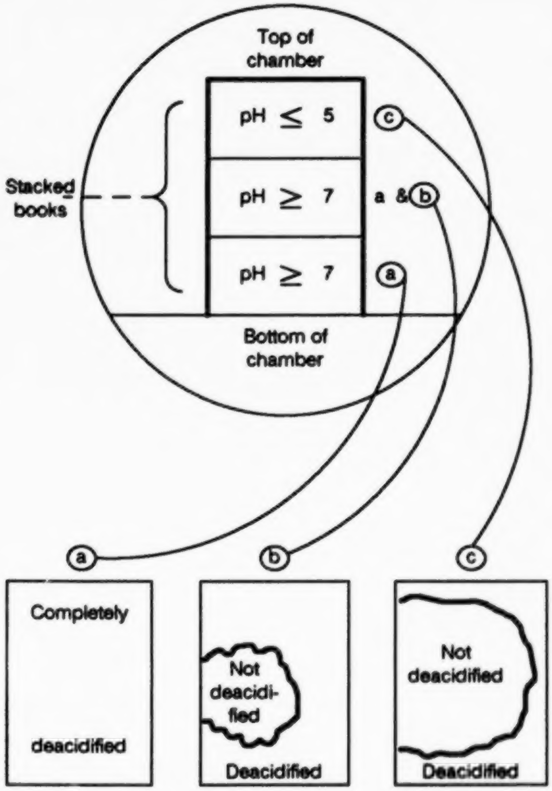
Table 6.—Results of the G.E. Tests for Uniform Treatment

				Exposure			
Batch	Book weight	DEZ mixture weight	Drying time (hours)	Pressure	Time	Qualitative results	Typical ZnO deposit[a]
1.	960#	32#	44¾	625 torr	24 hrs	Only partial deacidification	Books 1%, maps 1.85%
2.	881#	56#	89¾	25 torr 600 torr	26 hrs 114 hrs	Total deacidification	Books 0.573%, maps 2.7%
3A	1,086#	70#	117½	36 torr	29 hrs	Mixed—30% to 100% deacidification	Books 1.04%, single exposure
3B		30#	7	20 torr	24 hrs	Mixed—30% to 100% deacidification	Books 1.43%, maps 1.57%, double exposure
4.	820#	26# 16#	124	23 torr 43 torr	24 hrs 72 hrs	Total deacidification	

[a] Data based on deacidified portions—per George Kelly, Library of Congress.

SOURCE: General Electric, Valley Forge Space Center, Report to the Library of Congress, December 1978.

Figure 10.—NASA-5,000 Book Test, pH Results From Book Papers at Different Chamber Locations


Top of chamber
pH ≤ 5
pH ≥ 7
pH ≥ 7
c
a & b
a
Stacked books
Bottom of chamber
a
b
c
Completely deacidified
Not deacidified
Deacidified
Not deacidified
Deacidified

Typical page from a treated book from three locations shown

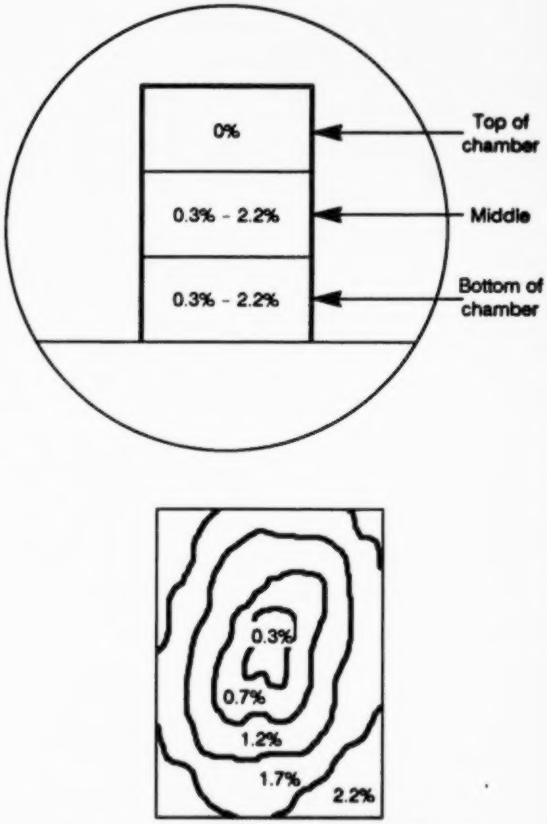
SOURCE: Library of Congress.

tion because DEZ appears to react rapidly and completely with the acids it contacts.

The complete and uniform deposition of 1.5 percent zinc oxide has been more difficult to achieve in large-scale tests. The G.E. tests did not achieve the 1.5 percent zinc oxide buffer with the amounts of DEZ and time provided. The 5,000-book NASA test achieved 2.2 percent zinc oxide in books located in the lower part of the chamber. But, similar to deacidification, the poor circulation of the DEZ affected the amount of zinc oxide that got deposited in books elsewhere in the chamber. Books in the middle of the chamber, which were effectively neutralized under the less than optimal treatment conditions had low and non-uniform deposition of zinc oxide. Furthermore, the pulsing of the DEZ into the chamber showed up as concentric rings of zinc oxide with varying concentrations. Outer rings had zinc oxide contents of 2.2 percent, while the inner rings had zinc oxide contents of less than 0.3 percent. As with deacidification, zinc oxide deposition occurs first on the outside edge of the outer pages and occurs last in the center of the center page. Books at the top of the 5,000-book chamber had no zinc oxide. (See figure 11.)

The changes made in the smaller scale NASA tests—i.e., the continuous feed of DEZ into the chamber at high rates to ensure good circulation—eliminated the zinc oxide rings, in fact figures 12 and 13 shows the uniformity that was achieved in

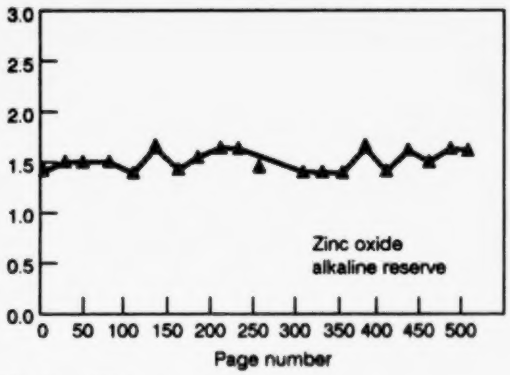
Figure 11.—NASA-5,000 Book Test, Zinc Oxide (%) Results From Book Papers at Different Chamber Locations


0%
0.3% - 2.2%
0.3% - 2.2%
Top of chamber
Middle
Bottom of chamber
0.3%
0.7%
1.2%
1.7%
2.2%

Typical book paper from a treated book located at middle or bottom of chamber

SOURCE: Library of Congress.

Figure 12.—Titrated Alkaline Reserve of Page v. Page Number for a 508-Page Book Treated in Experimental Run SST #13

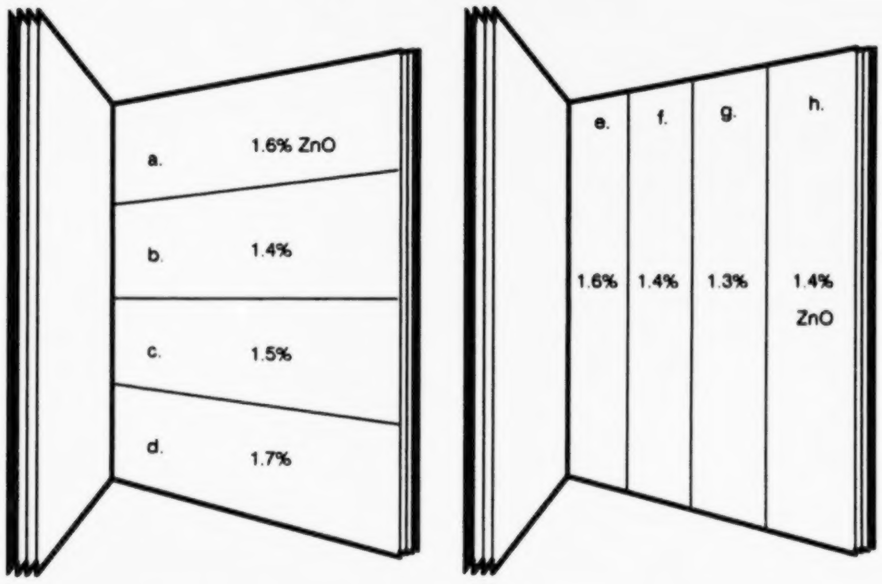


SOURCE: Library of Congress

one book in one of the final small-scale tests. These data were derived from randomly selected pages from randomly selected books from the small-scale runs. When placed under an ultraviolet light, zinc oxide deposition on these pages appeared uniform throughout a given book and independent of book location in the chamber.

The range in zinc oxide contents is the result of a number of factors. Not only does it depend on the amount of moisture left in the paper, but also on the amount of DEZ vapor available during treatment, time, and the type of paper being treated. Papers differ in the amount and type of cellulose that is used and the type of chemicals that have been added during, or remain after, manufacture. If any of these are acidic, additional DEZ will be needed for their neutralization. Characteristics of paper such as thickness, porosity, surface texture, etc. also affect the rate at which the DEZ can impregnate the paper. However, the data indicate that given enough DEZ and time, the desired zinc oxide buffer can be fairly uniformly deposited. The DEZ process appears to have excellent ability to uniformly neutralize acids and deposit 1.5 to 2.0 percent zinc oxide effectively. The variation in the amount of zinc oxide deposited in a variety of book papers treated in the same batch is being investigated at the pilot plant.

Figure 13.—Titrated Alkaline Reserve of One Page in a Book From Experimental Run SST #13



Top to bottom

Side to side

SOURCE: Library of Congress

Life Extension

The Library claims that DEZ treatment extends the life of books by three to five times. These claims are based on numerous fold endurance tests of treated and untreated paper. Tables 7 and 8 show the comparison for some of those papers treated for just 1 hour, and paper treated twice for 3 hours. These data indicate that the decline in fold endurance during aging appears to be slower in treated papers vs. untreated papers. Similar results from larger scale tests have been presented by the Library (see figures 14, 15, and 16).

How directly and accurately these fold endurance test results can be translated into a confident prediction of life extension for actual books treated is subject to debate. Tests on actual books many years after treatment may provide more confident predictions.

Table 7.—Drop in Fold Endurance Treated v. Untreated Paper (MIT test—0.5 kg)

	Equivalent years of aging[a]		
Paper	0	67	117
Newsprint:			
Untreated	118	3.5	0.6
Treated (1 hr.)	135	60	36
Mead bond:			
Untreated	465	92	54
Treated (1 hr.)	476	134	122
Offset GPO JCP-A60:			
Untreated	604	240	145
Treated (1 hr.)	652	441	315

[a] Aged at 90 °C at 50 percent relative humidity.

SOURCE: U.S. Patent #4,051,276.

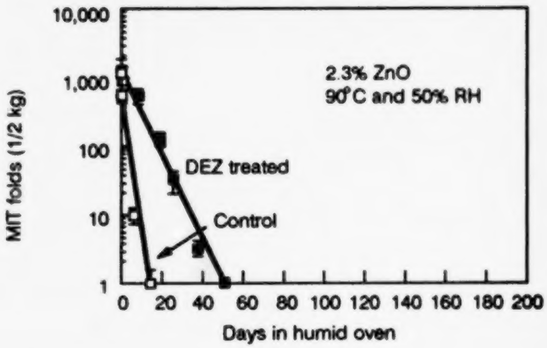
Table 8.—Drop in Fold Endurance Treated v. Untreated Paper (MIT test—0.5 kg)

	Days of aging[a]		
Paper	3	6	12
Newsprint:			
Untreated	54	8	0.9
Treated (total 3 hrs.)	65	48	41
JCP-A60 offset:			
Untreated	641	391	130
Treated (total 3 hrs.)	701	652	337

[a] Aged at 90 °C at 50 percent relative humidity.

SOURCE: U.S. Patent #4,051,276.

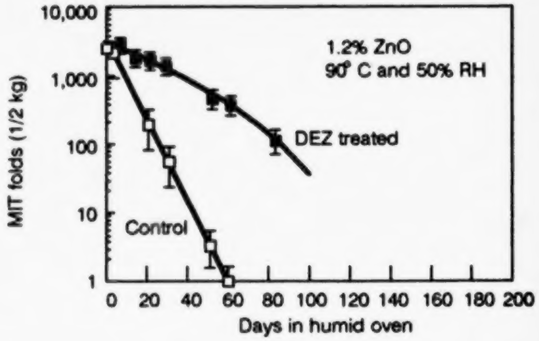
Figure 14.—MIT Folds (1/2 kg) v. Days in Humid Oven for Foldur Kraft Paper Treated in Experimental Run SST #6



Data points are means of 12 determinations; 99% confidence limits of means shown.

SOURCE: Library of Congress.

Figure 15.—MIT Folds (1/2 kg) v. Days in Humid Oven for Allied Superior Paper Treated in Experimental Run SST #4



Data points are means of 12 determinations; 99% confidence limits of means shown.

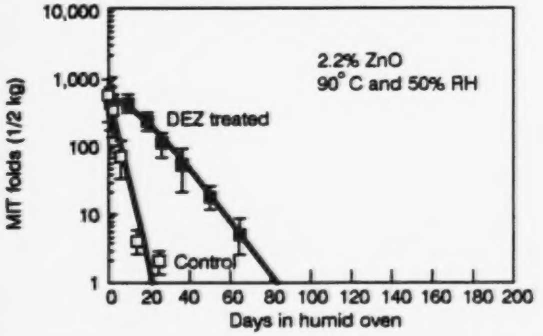
SOURCE: Library of Congress

Compatibility

In most cases, a paper's brightness does not appear to be affected by the DEZ treatment. In lab tests, the brightness remained virtually unchanged immediately after treatment and after aging.

Visual inspection of books treated in the larger scale tests showed no indication of incompatibility between the DEZ and other book materials. The Library also conducted two tests on 10 common book materials to determine whether DEZ reacted with these materials. First, a Fourier Transform

Figure 16.—MIT Folds (1/2 kg) v. Days in Humid Oven for Newsprint Paper Treated in Experimental Run SST #8



Data points are means of 12 determinations; 99% confidence limits of means shown.
SOURCE: Library of Congress.

Transmission Infrared Spectrum from a sample of each material was first generated. The material was then exposed to DEZ vapors, under process conditions, for 3 to 5 days. After exposure, a second infrared spectrum was taken. If any reaction between the material and the DEZ had taken place, the spectrum would have changed. Also, the temperature, pressure, and composition of the gas inside the test chamber was monitored to detect any evidence of a reaction. The other test was an x-ray fluorescence study. All but one of the materials tested negative, i.e., no reaction with DEZ was detected (see table 9). Nitro-cellulose, a material used in cloth book covers, did show some indication of reaction, resulting in clouding of the clear film. Some researchers have been concerned that the breakdown of nitro-cellulose can cause further degradation but the Library believes this is not a problem.

Zinc oxide can promote the photodegradation of paper under certain conditions.[3] The Library exposed treated and untreated papers to radiation from a sunlamp placed 24 inches from the paper in an oven at 60° C and 60 percent relative humidity. Specimens were then tested for fold endurance. The treated papers had much lower fold endurances. The Library does not consider this to be a major problem, however, since books are stored in such a way to minimize their exposure to light and ultraviolet radiation.

Table 9.—Reaction of DEZ Vapor With Various Book Materials

	Observations		
Material	FTIR Spectrum[a]	XRF[b]	Visual
Cellulose	No change	<0.5% Zn	No change
Lignin	No change	<0.5% Zn	No change
Gelatin	No change	<0.5% Zn	No change
Starch	No change	<0.5% Zn	No change
Polyvinylacetate	No change	<0.5% Zn	No change
Polyvinylalcohol	No change	<0.5% Zn	No change
Polyethylene	No change	<0.5% Zn	No change
Polypropylene	No change	<0.5% Zn	No change
Nitrocellulose	Small decrease—No	<0.5% Zn	Slight opacity
Fluorescent brighteners	—	—	Some decrease

[a] Fourier transform infrared.
[b] X-ray fluorescence.

SOURCE: Library of Congress.

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[3] George B. Kelly and John C. Williams, "Inhibition of Light Sensitivity of Papers Treated With Diethylzinc," presented at the Annual Meeting of the American Chemical Society, Washington, DC, September 1979.

DISCUSSION

The Library has developed a unique process that can uniformly neutralize the acids and deposit an alkaline reserve in books en masse. The process can deposit a uniform alkaline reserve independent of the variation in book acidity. Preliminary tests indicate that the process can also treat multiple formats.

The process appears to be compatible with inks, colors, pigments, and most other book materials, reducing the need to screen books for treatment and maximizing the number of books that can be treated. This conclusion is based on visual inspection, and includes two chemical tests that indicated DEZ does not react with 10 common book materials. The one exception is nitro-cellulose, a polymer material commonly used in book covers. The observed change is an increase in opacity in a clear film of the material.

OTA notes, however, that there is a lack of clear, documented, scientific understanding about what effect deacidification has on paper chemistry beyond the neutralization of acids and the deposition of alkaline buffers.

The Library contends that, though there may be some reactions undetected in their studies, the accelerated aging data on alkaline treated papers shows that undetected reactions do not appear to cause deterioration of the paper.

Of particular interest to some paper chemists is what effect the process has on the concentrations of cellulose functional groups that are capable of oxidizing and forming new acids. For example, it was hypothesized in the patent that DEZ may stabilize the cellulose's aldehyde groups. If this is so, an important source of new acid may be eliminated. More sensitive analysis may be able to determine whether this reaction actually occurs. The Library intends to conduct such studies in the future.

The chemical effects associated with deacidification will probably affect other degradation mechanisms. Oxidation is known to be affected by pH. Photodegradation, pollution, and biological attack may also be affected. The Library and others have raised the concern that zinc oxide increases the sensitivity of paper to photodegradation. Library tests to date have been inconclusive and a definitive evaluation of photodegradation is planned for during current pilot plant tests. However, since the Library collection is stored under very low ultraviolet light levels, they are less concerned about this problem than other libraries may be.

It is not clear to what extent the process will extend the life of the collection. The Library data suggest that the DEZ process can extend the life of a book by three to five times. The Library relies solely on fold endurance for demonstrating the improved life of treated paper. Although fold endurance is easy to determine and shows a measurable decline after accelerated aging, it is a very nonhomogeneous property and will vary considerably from sample to sample. Even averaging over a large number of specimens results in a large degree of uncertainty due to inhomogeneities within the paper.[4] This makes the significance of any data a critical test. On the other hand, fold endurance can be very useful and may be the best indicator of paper permanence if the tests are conducted carefully. The Library vigorously supports their approach to testing and evaluation as the most comprehensive, accurate, and appropriate to their needs.[5]

Some other scientists believe that a critical analysis lacking in the Library's assessment is the degree of polymerization. This is a direct measure of the physical integrity of the cellulose chains. A low degree of polymerization signifies that the cellulose chains have broken into small brittle lengths. It has been suggested that besides relying solely on fold endurance, tensile strength and zero-span strength also can be used to assess mechanical properties and that these could be combined with the degree of polymerization in an analysis of the process' effectiveness.

Another criticism is about the methods used by the Library in its accelerated aging experiments. The Library has been using a temperature of 90° C and both dry and humid conditions. Although the best temperature at which to age is debatable, it is generally believed that the lower the temperature, the better accelerated aging will simulate natural aging. Some paper chemists age at 80 ° C and only under humid conditions.

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[4] B.L. Browning, "The Application of Chemical and Physical Tests in Estimating the Potential Permanence of Paper and Papermaking Materials," *Preservation of Paper and Textiles* (Washington, DC: American Chemical Society, 1981), pp. 275-285.

[5] See app. D for suggested tests by the National Bureau of Standards.

The Library has not yet assessed the total impact the deacidification program will have on its collection, although this is also in their current plans. A variety of parameters affect the way papers respond to deacidification. These include the type(s) of fibers present, the types of fillers and other additives present, and the age of the paper and the state of chemical degradation that has already occurred. It is important, therefore, that the various tests performed to assess the effectiveness of the process be done on papers that are representative of the paper that will be treated. The Library has not sufficiently demonstrated that the fold endurance results are typical of those expected for their collection. Before the effectiveness of the deacidification program and the Library's current strategy can be fully assessed, some measurement of benefits must be made. This could be in terms of expected total book life saved or some other appropriate and measurable quantity.

Chapter 4

Costs

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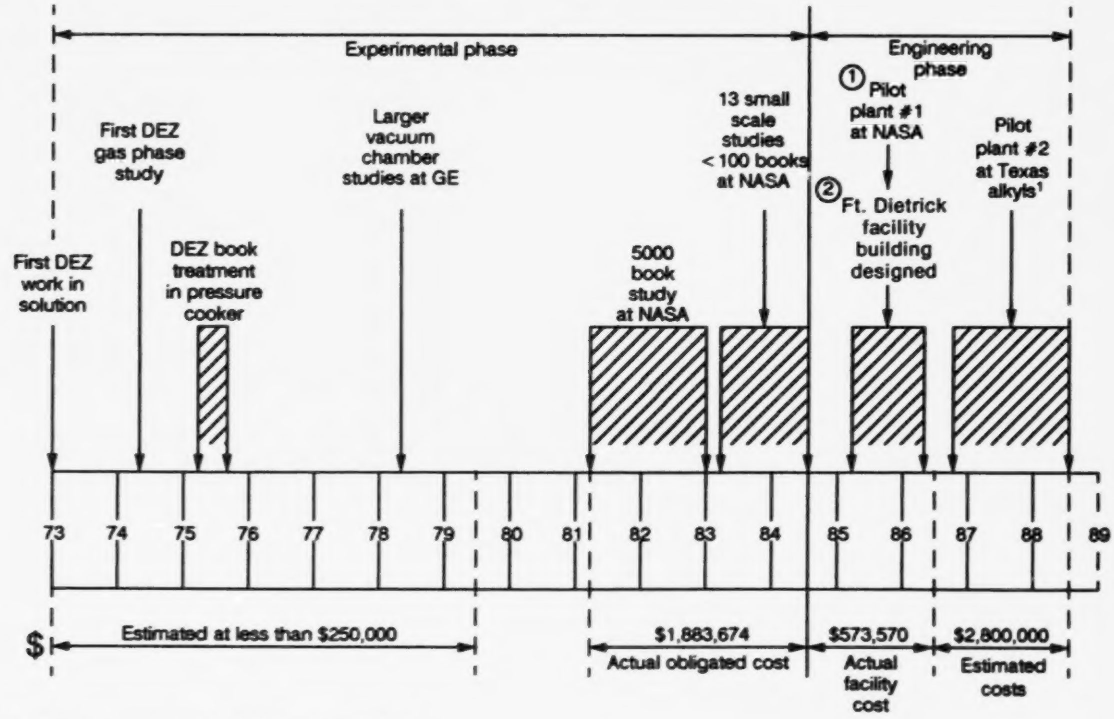
Chapter 4
Costs

INTRODUCTION

Since the Library of Congress' process for mass deacidification has been under development for the past 15 years, there have been a number of expenditures that could be categorized as research, development, and testing. Figure 17 displays those past expenditures that can be directly related to the Library's mass deacidification program from 1973 to 1988. It should be noted that certain of these expenditures have been for experiments whose purpose was a search for an optimum process and thus entailed comparison of various chemical treatments and results. Other expenditures were for experiments with the DEZ process alone and were directed toward learning the proper techniques for most effective results. The experimental phase can be considered to have ended with the completion of the 13 small-scale tests with books at NASA Goddard in late 1984. The Library of Congress reports that expenditures from 1973 through the end of this phase were about $2.1 million.

If another process were to be pursued for mass deacidification of the Library's collection some of the work already completed on the DEZ process would need to be repeated; other work may need to be repeated depending on the status of development of another process. For example, none of the alternative processes have been subjected to criti-

Figure 17. – DEZ Process Development History


Experimental phase
Engineering phase
First DEZ work in solution
First DEZ gas phase study
DEZ book treatment in pressure cooker
Larger vacuum chamber studies at GE
5000 book study at NASA
13 small scale studies < 100 books at NASA
① Pilot plant #1 at NASA
② Ft. Dietrick facility building designed
Pilot plant #2 at Texas alkyls¹
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$
Estimated at less than $250,000
$1,883,674
Actual obligated cost
$573,570
Actual facility cost
$2,800,000
Estimated costs

¹ Includes up to twenty operational experiments in pilot facility.

SOURCE: Library of Congress

cal independent evaluation of treated materials. The Library would most certainly need to compare accelerated aging tests (using standard papers), pH tests, alkaline buffer tests effects on library materials and others, test procedures, and protocols. It may also be necessary to evaluate certain aspects of safety, health, and environmental effects of another process. Therefore, expenditures for experimental work, while essentially completed for the DEZ process, would need to be increased if other chemicals, additional treatment, or new processes were to be considered.

Following the completion of the NASA small-scale tests, an expenditure of about $574,000 was devoted to the ill-fated first pilot plant. The Library of Congress considers that sum to be basically a loss to the Library, however, engineering and safety lessons were learned and have been applied to later work.

Starting in 1987 the Library of Congress' expenditures on the DEZ process can be directly related to engineering development, construction, and operation of the mass deacidification facility. For the purposes of this OTA evaluation, these expenditures can be put into three categories as follows:

1. Engineering Development Costs
   - —Design and Construction of Pilot Plant (Texas Alkyls)
   - —Hazard and Safety Review/Technology Management
   - —Initial Health & Environmental Studies
   - —Pilot Plant Test Program
2. Capital Costs—Full-Scale Facility
   - —Toxicological Risk Assessment
   - —Environmental Impact Assessment
   - —Plant Engineering and Architectural Design
   - —Plant Construction Management and Inspection
   - —Materials Handling—Engineering and Procurement
   - —Construction of Plant
   - —Commissioning and Startup Costs
   - —Contingency Costs
3. Facility Operating Costs
   - —Personnel—Plant Operations
   - —Personnel—Book Handling/Transportation
   - —DEZ Usage
   - —Utilities and Other Chemicals
   - —Maintenance Materials and Spares
   - —Operating Supplies
   - —Laboratory, Quality Control Costs
   - —Book Handling, Warehousing Expenses
   - —Insurance, Taxes and Other Indirect Costs
   - —Research Allowances and Contingency
   - —LOC Management Costs

To evaluate the per-book deacidification cost, OTA considers the first two categories above as capital costs and the third as annual operating costs. The total capital cost can be converted to an annual cost using an accepted rate of return over an assumed life of the project. For example, for a 10 percent[1] annual rate of return over a 20-year project life, a capital recovery factor[2] is 11.7 percent. Therefore, OTA chose to use a 12 percent capital recovery factor in arriving at a per book cost estimate.

The per-book cost of the DEZ facility will also vary considerably depending on the actual capacity or throughput finally realized when the plant is built. Since many costs (except for DEZ usage, certain labor, and supplies) will be fixed when the plant is operating, a large increase in capacity will result in a substantial decrease in per-book costs. Therefore, one of the goals of the pilot plant test program is to reduce the cycle time (and thus increase the plant capacity) to the most cost-effective level. The optimum cycle time will not be determined until a series of tests are completed in mid-1988. This study therefore assumes a capacity of 1 million books per year for the full-scale plant when estimating per-book costs.

The actual construction costs for the full-scale plant are also subject to some uncertainty. Major decisions on plant configuration—such as the size and number of treatment chambers—will not be made until some pilot plant tests are completed and a design study is done. Also the engineering design of the full-scale plant will not be started until mid-1988. Therefore, capital cost estimates must be considered only preliminary numbers for budgetary purposes. Plant operating cost estimates, however, may not be subject to as much variation only because the major cost categories (labor, DEZ usage, overhead) will not change significantly even if plant design changes are made. However, over the 20-year life of the plant these costs will undoubtedly change depending on inflation, possible plant improvements needed, and changes in chemical costs.[3]

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[1] Approximately the current rate for long-term government bonds.

[2] An annual payment that will repay a loan in X years with compound interest on the unpaid balance.

The following sections of this chapter present and discuss the cost estimates that have been prepared by the Library of Congress for design, development, construction, and operation of the DEZ mass deacidification facility. Part II of this report presents available data for alternative processes. While it is difficult to make cost comparisons because very little of the data are comparable in terms of accuracy and completeness, OTA has made some initial comparative comments. One basis of comparison is on the pilot plant level. It should be noted that the Library of Congress' pilot plant at Texas Alkyls has a capacity of about 50 books per 8-hour shift using a 55-hour cycle time even though much of the machinery is sized for a much larger capacity.[4] This could possibly be compared (with some caution) to the Canadian Library plant with a present capacity of 150 books per 8-hour shift; and with a pilot plant designed, but not built, by the Koppers Co. with a projected capacity of 100 books per 8-hour shift. Such a comparison is very rough at this time, but, when two or more pilot plants of roughly similar capacity begin obtaining actual operating history, more accurate cost comparisons could be made.

Photo credit: Library of Congress

DEZ pilot plant at Texas Alkyls

COST ESTIMATES FOR THE DEZ FACILITY

Engineering Development

The costs for engineering development for the LOC deacidification facility have been assumed by OTA to include all work associated with designing, constructing, and testing the second pilot plant at Texas Alkyls. As of this writing, most of those costs are quite firm but the number of tests (and thus the costs of tests) may vary before they are completed in mid-to-late 1988. Table 10 displays the estimated costs of engineering development that were supplied by the Library to OTA.

Table 10.—LOC Engineering Development Cost Estimate for DEZ Mass Deacidification Program

Pilot plant design and construction	$1.9 million
Pilot plant test program	0.8 million
Other	0.1 million
Total	$2.8 million

NOTE: These costs were incurred and obligated in 1987 and 1988.

SOURCE: Library of Congress.

Capital Costs—Full-Scale Facility

At OTA's request the Library of Congress prepared a capital cost estimate for the full-scale deacidification facility. That estimate is in appendix C of this report. Table 11 summarizes the LOC cost estimate. Several categories are not included in the LOC estimate. OTA believes the costs could vary considerably because of the number of unknowns about the facility at this time. OTA also believes the cost estimates are low; OTA advisors are concerned that the plant design assumptions are

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[3] OTA has not investigated possible cost changes for DEZ but notes that only one supplier now produces the chemical and future prices will largely be determined by that supplier. One or two other suppliers could produce DEZ and have in the past, but the market is not now attractive for them.

[4] The DEZ pilot also has a number of purposes and its design was based on the need to conduct a wide range of experiments as well as engineering tests. Comparisons with other plants, without such design constraints, must therefore take this into account.

Table 11.—LOC Capital Cost Estimate for 1 Million Books/Year Deacidification Facility

Item	Cost ($ millions)
Building cost	1.8
Site work	0.3
Chemical process facility	2.8
Total LOC estimate	4.9

NOTES: 1. Costs based on assumption of two separate structures—a support building and a chemical treatment facility.
2. Chemical plant cost is based on a hypothetical chamber size for four chambers.
3. Chemical plant assumes hardware similar to pilot plant.
4. Not included in estimate are: utilities, site development, emergency power, contingency.
5. Plant assumed to be located at Ft. Detrick, MD.

SOURCE: Library of Congress.

Table 12.—LOC Operating Cost Estimate for 1 Million Books/Year Deacidification Facility

Item	Annual operating cost ($ millions)
Plant costs (chemicals/supplies/utilities)	1.0
Operating labor	0.6
Plant overhead	0.1
Administrative costs	0.1
Total LOC estimate	1.8

NOTES: 1. Operations are 24 hours/day, 350 days/year.
2. Plant assumed to be located at Ft. Detrick, MD, and thus no costs are included for taxes, insurance, safety and fire protection, etc.
3. Contractor supervision and operation is assumed with fee for this at 15 percent of labor cost.
4. No costs are included for book handling and transportation to and from the Library but this was estimated at $0.70 per book.

SOURCE: Library of Congress.

too optimistic (e.g., a 36-hour cycle time and few backup systems); OTA is concerned because the full-scale chemical plant cost appears low if compared with budgetary scale-up factors which are used as rough guidelines in the chemical industry. OTA has not, however, prepared an independent cost analysis and therefore its comments on costs must be considered only as cautionary.

Facility Operating Costs

Table 12 is a summary of LOC estimates of annual operating costs for the full-scale facility with an assumed capacity of 1 million books per year. (See app. B for the LOC estimates and assumptions.)

OTA reviewed these costs and considers several of the categories to be too low. First, projected labor costs are considered low because they do not make enough allowances for overtime, maintenance, training, turnover, and contingency. Second, the contractor's fee is considered low because of the special requirements for experience and competence. Third, costs for Fort Detrick services (e.g., security, grounds maintenance, safety, and fire protection) are not included; nor are costs for staff training, drills, and skills upgrading. Finally, book handling and transportation costs are not included although previous estimates of these costs are noted. OTA advisors also were concerned that insurance against an accident did not show up as a cost or a contingency; and that no allowance was made for possible increases in the cost of DEZ.

DISCUSSION

There are several difficulties with analyzing the available cost estimates for the DEZ mass deacidification process. First, a number of design and program management decisions are yet to be made and these could affect costs substantially. Second, the cost data presented by LOC does not include some possible major costs such as book transportation and handling, plant commissioning, and contingencies. Third, the LOC estimates appeared to be on the low side when reviewed by OTA's advisors. Finally, a consistent method for projecting total costs and per-book costs has not been determined.

OTA believes it is important to develop a consistent method and accurate cost projections with contingencies as soon as possible. Such projections are important to decisions (yet to be made) about size or capacity of the full-scale plant. They are also important if any of the possible alternative processes are to be evaluated. At present it appears that at least two alternative processes would have much lower costs than the DEZ process but this conclusion is based on incomplete cost data and no consistent method for comparison.

Even though it may not be accurate, OTA prepared its own very rough estimate of the DEZ program total costs to determine a possible range of per book treatment cost that may be applied if all elements are included. This estimate was made only for the purpose of this report. New data could change it. Final per-book costs are presented as a ± 20 percent range because of the uncertainties involved.

Table 13 displays the OTA estimate of capital costs, operating costs, and per-book costs.

To derive a total capital cost estimate OTA included the engineering development costs and the toxicological risk assessment costs. OTA then made rough estimates of materials handling facilities, and commissioning costs. OTA also added about a 6 percent contingency.

To derive a total operating cost estimate, OTA added about 10 percent more labor costs, a higher contracting fee, and a fee for Ft. Detrick services to the LOC estimate. OTA then added a book handling and transport cost based on an earlier LOC estimate.

For a very rough estimate of per-book costs of deacidification at the LOC facility, OTA has included engineering development and plant construction in one total capital cost estimate. We then assumed a 12 percent per year capital recovery factor for this total and added the annual facility operating cost to that. The total per book treatment costs thus determined are from $3.50 to $5.00 per volume. A number of OTA advisors believe that the higher ($5.00) per-book cost is the most realistic but without a more systematic and detailed estimate this cannot be confirmed.

Table 13.—OTA Capital and Operating Cost Estimates for 1 Million Books Per Year Deacidification Facility

Capital cost:	
LOC estimate	$ 4.9 million
OTA additions:	
Toxicological risk assessment	1.5
Transport and materials handling	0.5
6-month commissioning	0.9
Contingency	0.5
Engineering development	2.8
Total capital cost	$11.1 million
Annual operating costs:	
LOC estimate	$ 1.8 million
OTA additions:	
Added labor	0.1
Added contractor fee	0.1
Ft. Detrick services	0.1
Book handling and transportation	0.7
Total operating costs	$ 2.8 million
Per-book costs:	
Total capital	$11.1 million
Annual capital recovery @ 12 percent	1.3 million
Annual operating costs	2.8 million
Per-book cost @ 1 million books/year =	$4.1
±20-percent range of per-book cost =	$3.50-$5.00

SOURCE: Office of Technology Assessment, 1988.

Chapter 5

Safety

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Chapter 5

Safety

INTRODUCTION

One of the most serious concerns with the Library of Congress' program and the DEZ process has been safety. Because of the attention given to the accident during tests at NASA Goddard in 1986, many critics focused on the question of whether DEZ could be handled safely in the future. This chapter discusses the hazards that are present and the effort the Library has made and must continue to make to manage those hazards to ensure the safe operation of a full-scale plant.

HAZARDS

DEZ is considered a hazardous material. It is very reactive with certain compounds and is capable of releasing large amounts of energy. Fire is the principal hazard and, under certain specific conditions, explosions could occur.

DEZ is pyrophoric, meaning it will spontaneously ignite if it comes in contact with air (or, more specifically, the oxygen in air). The reaction is very fast, and releases a great amount of heat. The intensity of the heat is itself a hazard. It could ignite flammable materials nearby, cause damage to nearby structures or property, or cause injury directly. The byproducts of the reaction, carbon dioxide, water, and zinc oxide, are stable. Large leaks or spills of DEZ could pose a significant fire hazard. The product of DEZ reactions (ethane gas) can reach an explosive mixture with air. Under certain conditions, in unvented containers, DEZ reactions can also cause a pressure buildup which could cause an explosive rupture of the container.

DEZ is also very reactive with water. The byproducts are ethane gas and zinc oxide. If liquid DEZ and liquid water come into contact, the reaction that takes place can be very vigorous, releasing large amounts of ethane gas very quickly. The reaction between DEZ vapors and water vapor is not as vigorous, especially the reaction between DEZ vapor and absorbed water that takes place within books during deacidification.

The reaction between DEZ and water also releases heat. Although the amount of heat that is released is about 10 times less than the amount released during a reaction between DEZ and air, it is enough to require careful monitoring during deacidification. During normal book treatment conditions, within a processing chamber, the DEZ vapor is circulated at very low pressures and any reactions with air has been shown to result in only small temperature increases and no flames or pressure increases. Tests to confirm this have been done by the Library.

DEZ will begin to decompose at 120° C, into hydrogen, ethane or other hydrocarbons, and zinc. Heat is again released. At 150° C, decomposition becomes autocatalytic. This means that the heat released will cause decomposition to proceed on its own and prevent it from being stopped. Autocatalytic decomposition of liquid DEZ would result in a very rapid and uncontrollable release of gases. Monitoring and controlling DEZ gas temperature in the process becomes critical to prevent the decomposition of DEZ. Early tests with the Houston pilot plant show adequate DEZ temperature control is possible within safe ranges to prevent autocatalytic decomposition.

The rapid release of gases associated with the decomposition of DEZ and with reactions between DEZ and water pose a significant hazard. If they occur in a contained environment, the resulting overpressure situation could cause rupture and subsequent fire. Storage vessels in a processing plant must therefore be designed with pressure relief systems. Explosion is a potential hazard because under certain conditions both ethane and hydrogen gas mixtures with air are explosive.

Photo credit: Library of Congress

Hooking up DEZ for NASA 5,000-book test

The amount of DEZ that will be used at the deacidification plant (up to 3,900 pounds in storage, and approximately 50 pounds per treatment) limits the scope of these hazards. Large numbers of people will not be at risk. However, they do pose significant risks for plant operators, safety personnel, and the immediate surrounding property. Such risks can be managed with proper attention to design and safe operating practices. As an example, the Library intends to locate DEZ storage containers at a distance away from the chemical plant and provide barriers to contain a potential fire.

SAFETY—A CRITICAL ISSUE

The potential for fire and explosion associated with the use of DEZ makes safety a critical issue for the DEZ process. The basic goal of safety management is to eliminate or reduce to an acceptable level the risk of injury or damage to personnel, material, or property associated with a given hazard.

There is a generally accepted priority to reducing the risk to personnel and property:

1. eliminate or reduce the hazard through design and operations,
2. isolate the hazard,
3. train personnel to operate around the hazard, and
4. provide protective and emergency systems and procedures.

The use of DEZ precludes eliminating the hazards associated with it. However, the relatively safe manufacture of DEZ by Texas Alkyls, Inc., and its use in a number of applications over the last 20 years suggests that the risks can be kept at acceptable levels. This requires a good understanding of the chemical and physical properties of the materials and processes involved, good design, detailed and safe operating procedures (including inspection and maintenance procedures), experienced operators who receive continuous training in operational and emergency procedures, and a good safety review program.

The importance of these issues as they relate to the DEZ process can be seen by reviewing the events leading to the failure of the first pilot plant. The following discussion is based on the NASA Accident Investigation Board's Report and discussion with NASA and Northrup personnel.

Importance of Safety—The Goddard Accidents

Construction of the first DEZ pilot plant at NASA's Goddard Space Flight Center was completed in October of 1985. System checks were initiated in October. The first full-scale test, a complete cycle but without the books, was initiated on December 5. Immediately upon initiating the rehydration phase of that operation, by introducing liquid water into the chamber, the pressure rose forcing the door open and a fire broke out in the chamber. There were two people in the processing area at the time, but there were no injuries. The fire burned itself out quickly, but not before causing extensive damage to the chamber and surrounding instrumentation and hardware.

The system was secured and the power turned off. Cleanup and repairs proceeded through January. In February, procedures were drafted for deactivating the system and to resume testing.

When the system was turned on, a pressure buildup in the line between a condenser and the brine seal tank was detected (see figure 18). The pressure buildup exceeded the range of the pressure gauge for that line. The deactivation procedures were then revised to include relieving the pressure in the line by first testing the valves for operability, and then to progressively pump the system to vacuum.

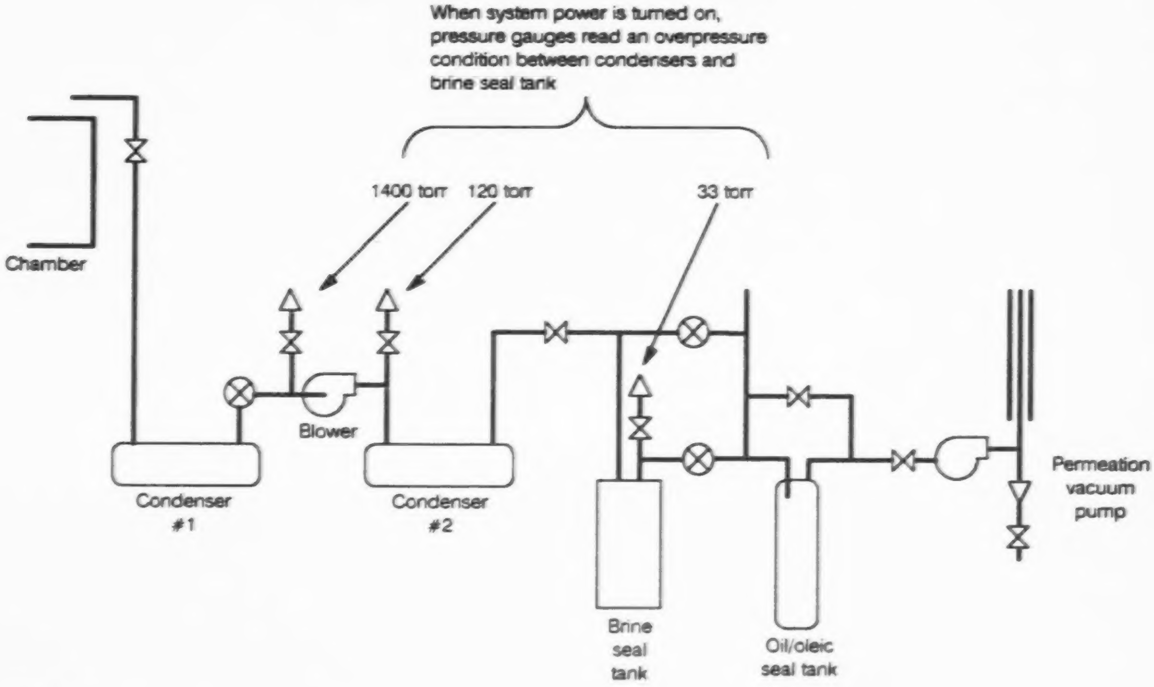
Valves were tested, beginning at the vacuum pump, and leading back toward the condenser. When the valve between the condenser and the brine seal tank was cycled, contents from the brine seal tank squirted out from a defective seal in the tank (see figure 19). The seal tank was replaced, and the valve tests completed. The system was then progressively pumped to vacuum. When a valve in a section of line upstream from the condenser was opened, an explosion occurred in the line between the condenser and the brine seal tank, and a second fire broke out (see figure 20). The explosion was of sufficient force to blow out two doors in the processing area. The subsequent fire burned out quickly, but caused substantial damage to the plant and surrounding area. There was one person in the processing area at the time of the accident, but there were no injuries.

The system remained in an unstable condition. After careful consideration of how to proceed, an army demolition team was called in to dismantle the plant.

The apparent cause of the first fire was the presence of liquid DEZ in the chamber. When water was introduced, the reaction with the DEZ rapidly evolved ethane gas which blew the chamber door open. With the door open, air came into contact with the DEZ and the fire started.

It is not known for certain how liquid DEZ came to be in the chamber. The apparent cause was condensation of DEZ in the vapor line leading into the chamber. The line heater for that section of the line

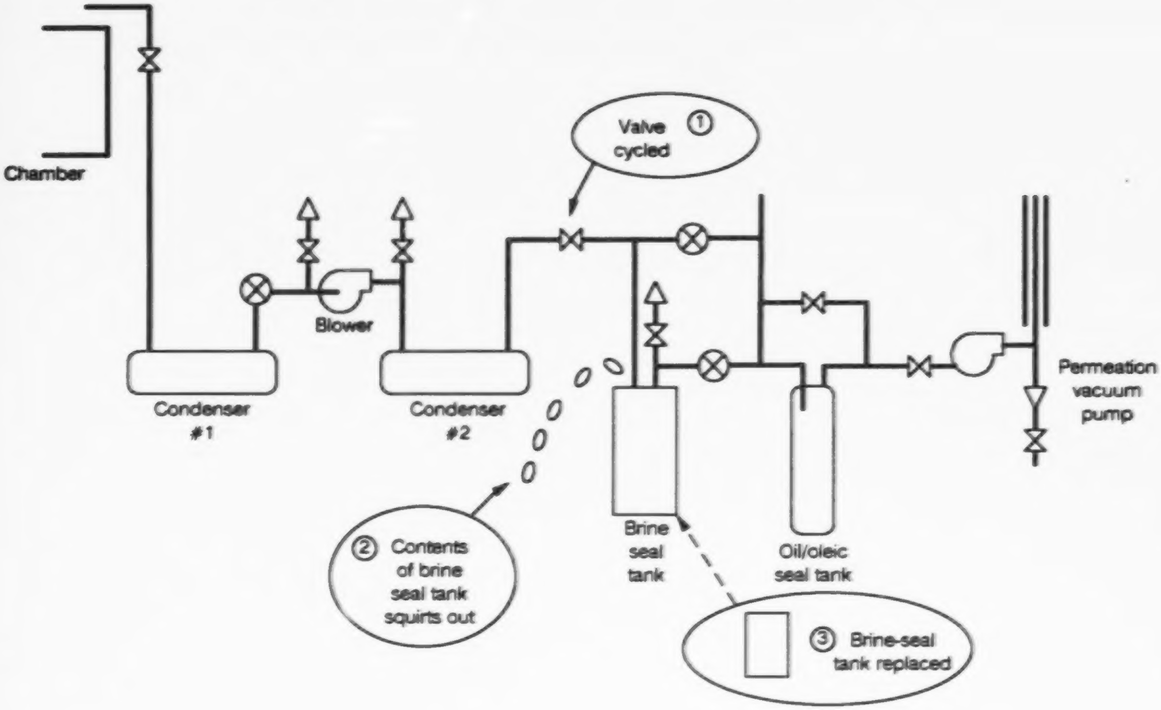
Figure 18.—Chronology of Second Goddard Incident



When system power is turned on, pressure gauges read an overpressure condition between condensers and brine seal tank

SOURCE: Office of Technology Assessment, 1988

Figure 19.—Chronology of Second Goddard Incident (continued)



SOURCE: Office of Technology Assessment, 1988

was working intermittently, and some of the insulation around the line was missing. Due to the configuration of the line as built, liquid DEZ ran into the chamber instead of away from the chamber.

The explosion and second fire were apparently caused by brine and liquid DEZ reacting in the condenser. Evidence of brine was found in the condenser, and probably backstreamed into the condenser when the defective brine seal was replaced. Liquid DEZ must have been present upstream from the condenser. When the upstream valve was opened, the liquid DEZ traveled down the line and into the condenser, and reacted with the brine. The reaction rapidly produced a large amount of ethane which ruptured the line and caused the fire.

The presence of liquid DEZ in the line was supported by the fact that over 700 pounds of DEZ was pumped into the system, instead of the 30 pounds called for in the test. This was not immediately known, however, because the DEZ tanks were not on load cells as called for in the design. It wasn't until after the first accident that the tanks were weighed and the discovery was made. The presence of excess liquid DEZ in the system explains the pressure buildup that occurred while the system was being repaired.

The general conclusion of the NASA Accident Investigation Board[1] was that no one involved "fully appreciated the engineering challenges" associated with scaling up the continuous DEZ feed and recycling system. The care and diligence that went into the design and operation of the 5,000-book test was not carried forward to the NASA pilot plant development.

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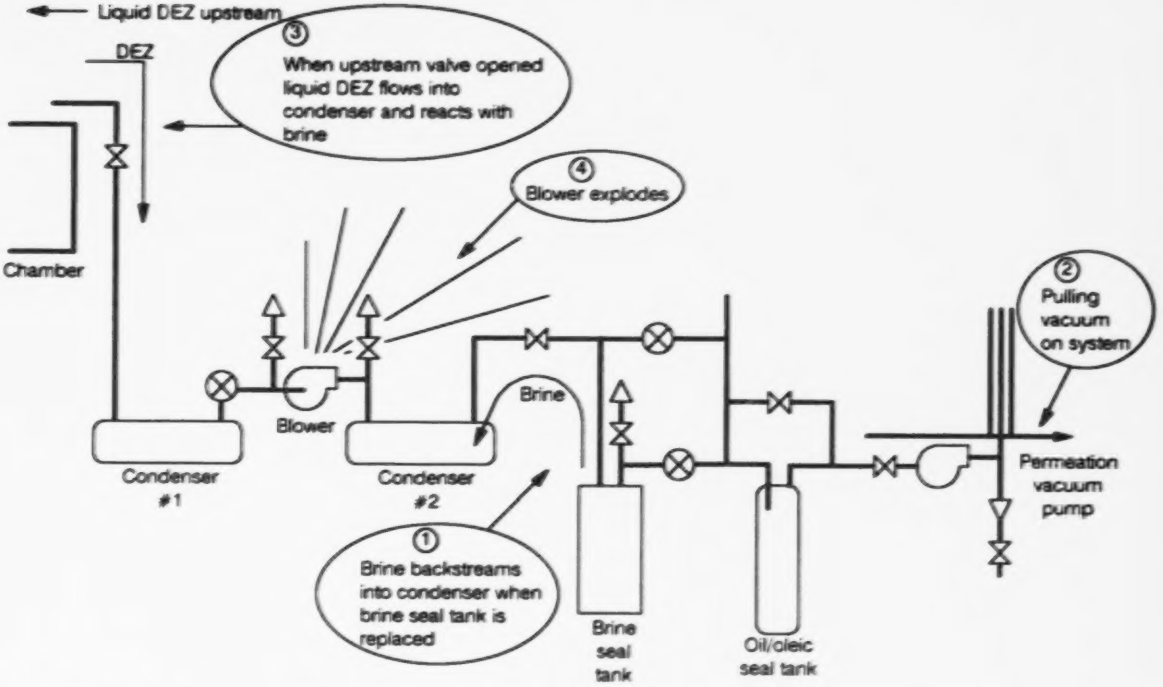
[1] Accident Investigation Board Report on the Mishaps at the Deacidification Pilot Plant, Building 306, on Dec. 5, 1985 and Feb. 14, 1986; Sept. 4, 1986.

Figure 20. – Chronology of Second Goddard Incident (continued)


Liquid DEZ upstream
DEZ
③ When upstream valve opened liquid DEZ flows into condenser and reacts with brine
④ Blower explodes
Chamber
② Pulling vacuum on system
Brine
Blower
Condenser #1
Condenser #2
Permeation vacuum pump
① Brine backstreams into condenser when brine seal tank is replaced
Brine seal tank
Oil/oleic seal tank

SOURCE: Office of Technology Assessment, 1988

More specifically, the board came to the following conclusions:

(Excerpt from the NASA accident report)

There was a lack of appropriate instrumentation. In general, the system was under instrumented. Pressure gauges did not have a high enough range to monitor overpressure situations. There were no pressure relief valves in the lines, and most notably none in the chamber. Venting of the chamber was through the door. The use of semi-automatic valves required that personnel be present in the processing area during an operation. Also, real time monitoring of the system would be more appropriate. The presence of liquid DEZ in the chamber was actually picked up by a thermocouple reading at the bottom of the chamber. It was recorded on a strip chart but not monitored by the controller.

There was a failure to install the instrumentation called for by the plant design. The failure to place the DEZ tanks on load cells was a serious oversight. With a substance as hazardous as DEZ, an accurate inventory must be kept.

There was a failure to develop and follow procedures. The contract between Northrup and NASA requires the development of at least five procedures; a facility operating procedure that gives detailed operating instructions for both normal and emergency situations, an operations test procedure that gives special instructions pertinent to the test at hand, a pre-start check list, an operations log which records all significant events during operation, and an engineering log that also records all significant events and all activities and calculations pertaining to the test. The systems tests begun in October and the full- scale test in December were run without test procedures. No operations or engineering logs were kept. Furthermore, deactivating of the system began before the clean-up procedures were approved, and they were revised without review. Also, the poor condition of the insulation on the vapor line leading into the chamber indicated that there was inadequate routine inspection of the system.

There was one significant design deficiency, the piping configuration allowed liquid DEZ to flow into the chamber rather than away from the chamber. The use of a brine seal tank is questionable.

In the 5000 book test, brine seal tanks were advised against, because of the violent reaction that occurs between DEZ and brine.Finally, normal safety procedures were compromised. A Failure Mode and Effects Analysis was carried out and presented to a NASA review board. The analysis was accepted and operation approved. However, there was no documentation of who received and approved the report.

Only the results of the analysis were presented to the board with little or no documentation or explanation. Approval was granted although necessary procedures were not available. The analysis was not submitted for outside review. And there was no verification or inspection of the final contruction and installation.

The accident investigation board made the following recommendations:

- The plant should be more fully instrumented, especially in regards to monitoring the inventory of DEZ. It should also allow remote operation of the system.
- The process should be controlled by an automated process controller to provide real time monitoring and display and to operate safety interlocks.
- The design, construction, and operations of the plant should be subjected to a third party review.

Importance of Safety—Accident at Ethyl Corp.

Another example of the potential hazards associated with metal alkyls is an accident that occurred at an Ethyl Corp. facility in 1986. Ethyl is also a major producer of metal alkyls and the only other domestic supplier of DEZ (although they have not produced DEZ in recent years). During the manufacture of a metal alkyl product, a large explosion occurred. Although details of the accident are not publicly available, there were some injuries, the damage was extensive, and the plant had to be rebuilt.

SAFETY AT THE TEXAS ALKYLS PILOT PLANT

This section discusses the safety of the Texas Alkyls pilot plant by examining the actions taken by the Library and its contractors in the following areas: understanding of the physical and chemical properties of all reactants and products; design-for-safety; operational safety; safety management and review. The deficiencies noted in the first pilot plant effort have been addressed and the margin of safety improved. However, whether the actions have been sufficient can only be demonstrated by repeated testing of the system.

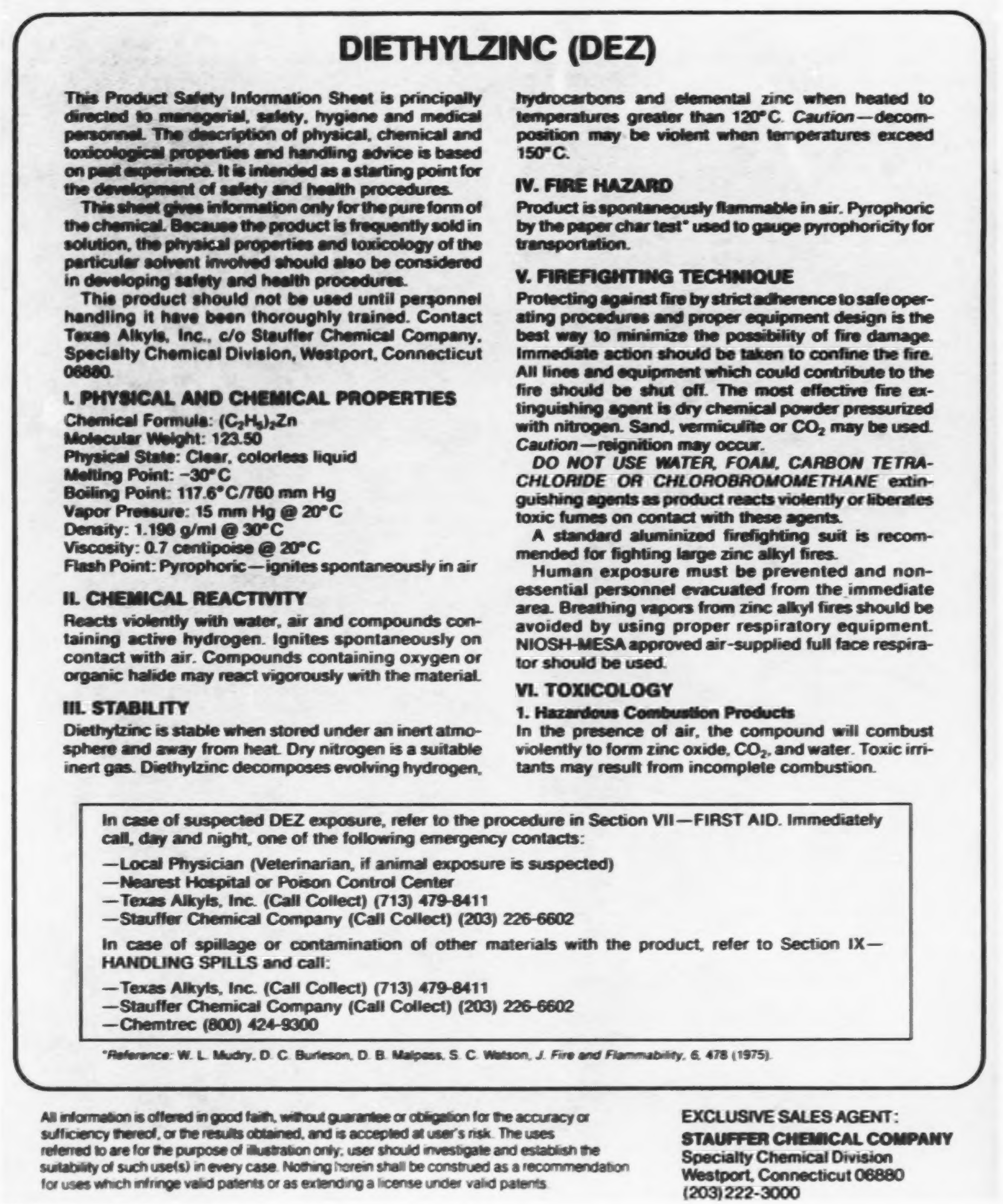
Understanding the Physical and Chemical Properties of Products and Reactants

It is important to know as much as possible about the physical and chemical properties of all the materials involved in a process and to understand the thermodynamic and thermochemical properties of all possible reactions. Of particular importance is the amount of energy released during various reactions and the stability of the reactants and products in the presence of that energy. The physical and chemical properties of DEZ, and its reactions with other compounds have been studied for many years. Texas Alkyls' sales brochure for DEZ lists some of these properties and reactions. Critical safety information is available in the Product Safety Information Data Sheet (see figure 21).

As mentioned DEZ is pyrophoric. The heat of combustion is high. DEZ is also very reactive with free hydrogen ions, hence its reactivity with acids and water. These reactions are fairly well-understood. Stauffers (one of Texas Alkyls' parent companies) has done some additional experiments with liquid DEZ and liquid water reactions, measuring the amount of ethane that is evolved.

According to tests performed by the Library, DEZ does not react with most book materials. In particular, the Library has concluded that DEZ

Figure 21.—Product Safety Information Sheet for Diethylzinc



DIETHYLZINC (DEZ)

This Product Safety Information Sheet is principally directed to managerial, safety, hygiene and medical personnel. The description of physical, chemical and toxicological properties and handling advice is based on past experience. It is intended as a starting point for the development of safety and health procedures.

This sheet gives information only for the pure form of the chemical. Because the product is frequently sold in solution, the physical properties and toxicology of the particular solvent involved should also be considered in developing safety and health procedures.

This product should not be used until personnel handling it have been thoroughly trained. Contact Texas Alkyls, Inc., c/o Stauffer Chemical Company, Specialty Chemical Division, Westport, Connecticut 06880.

I. PHYSICAL AND CHEMICAL PROPERTIES

Chemical Formula: $(C_2H_5)_2Zn$
Molecular Weight: 123.50
Physical State: Clear, colorless liquid
Melting Point: −30°C
Boiling Point: 117.6°C/760 mm Hg
Vapor Pressure: 15 mm Hg @ 20°C
Density: 1.198 g/ml @ 30°C
Viscosity: 0.7 centipoise @ 20°C
Flash Point: Pyrophoric—ignites spontaneously in air

II. CHEMICAL REACTIVITY

Reacts violently with water, air and compounds containing active hydrogen. Ignites spontaneously on contact with air. Compounds containing oxygen or organic halide may react vigorously with the material.

III. STABILITY

Diethylzinc is stable when stored under an inert atmosphere and away from heat. Dry nitrogen is a suitable inert gas. Diethylzinc decomposes evolving hydrogen, hydrocarbons and elemental zinc when heated to temperatures greater than 120°C. *Caution*—decomposition may be violent when temperatures exceed 150°C.

IV. FIRE HAZARD

Product is spontaneously flammable in air. Pyrophoric by the paper char test* used to gauge pyrophoricity for transportation.

V. FIREFIGHTING TECHNIQUE

Protecting against fire by strict adherence to safe operating procedures and proper equipment design is the best way to minimize the possibility of fire damage. Immediate action should be taken to confine the fire. All lines and equipment which could contribute to the fire should be shut off. The most effective fire extinguishing agent is dry chemical powder pressurized with nitrogen. Sand, vermiculite or CO_2 may be used. *Caution*—reignition may occur.

DO NOT USE WATER, FOAM, CARBON TETRACHLORIDE OR CHLOROBROMOMETHANE extinguishing agents as product reacts violently or liberates toxic fumes on contact with these agents.

A standard aluminized firefighting suit is recommended for fighting large zinc alkyl fires.

Human exposure must be prevented and nonessential personnel evacuated from the immediate area. Breathing vapors from zinc alkyl fires should be avoided by using proper respiratory equipment. NIOSH-MESA approved air-supplied full face respirator should be used.

VI. TOXICOLOGY

1. Hazardous Combustion Products

In the presence of air, the compound will combust violently to form zinc oxide, CO_2, and water. Toxic irritants may result from incomplete combustion.

In case of suspected DEZ exposure, refer to the procedure in Section VII—FIRST AID. Immediately call, day and night, one of the following emergency contacts:

—Local Physician (Veterinarian, if animal exposure is suspected)
—Nearest Hospital or Poison Control Center
—Texas Alkyls, Inc. (Call Collect) (713) 479-8411
—Stauffer Chemical Company (Call Collect) (203) 226-6602

In case of spillage or contamination of other materials with the product, refer to Section IX—HANDLING SPILLS and call:

—Texas Alkyls, Inc. (Call Collect) (713) 479-8411
—Stauffer Chemical Company (Call Collect) (203) 226-6602
—Chemtrec (800) 424-9300

*Reference: W. L. Mudry, D. C. Burleson, D. B. Malpass, S. C. Watson, *J. Fire and Flammability*, 6, 478 (1975).

All information is offered in good faith, without guarantee or obligation for the accuracy or sufficiency thereof, or the results obtained, and is accepted at user's risk. The uses referred to are for the purpose of illustration only; user should investigate and establish the suitability of such use(s) in every case. Nothing herein shall be construed as a recommendation for uses which infringe valid patents or as extending a license under valid patents.

EXCLUSIVE SALES AGENT:
STAUFFER CHEMICAL COMPANY
Specialty Chemical Division
Westport, Connecticut 06880
(203) 222-3000

SOURCE: Texas Alkyls, Inc.

2. Ingestion

Because of the highly reactive nature of this compound with air, ingestion is highly unlikely (See Skin Contact).

3. Inhalation

Because of the highly reactive nature of this compound with air, inhalation of this compound is highly unlikely.

4. Skin Contact

Concentrated product will react immediately with moisture on the skin to produce severe thermal and chemical burns.

5. Eye Contact

Concentrated product will react immediately with moisture in the eye to produce severe chemical and thermal burns.

6. Threshold Limit Value (TLV)

There is no TLV for the product because the compound does not exist in air.

VII. FIRST AID

If a known exposure occurs, immediately initiate the recommended procedures below. Simultaneously *Contact a Physician.* Describe the type and extent of exposure and symptoms.

1. Eye Contact

Immediately flush the eyes with large quantities of running water for a minimum of 15 minutes. Hold the eyelids apart during the irrigation to ensure flushing of the entire surface of the eye and lids with water. Do not attempt to neutralize with chemical agents. Obtain medical attention as soon as possible. Oils or ointments should be used only on the advice of a physician. Continue the irrigation for an additional 15 minutes if the physician is not immediately available.

2. Skin Contact

Immediately remove contaminated clothing under a safety shower. Flush all affected areas with large amounts of water for at least 15 minutes. Do not attempt to neutralize with chemical agents. If ice is available, apply locally to the affected area. Obtain medical advice immediately.

3. Inhalation

Exposure to combustion products may cause respiratory symptoms. Remove from contaminated atmosphere. If breathing has ceased, clear the victim's airway and start mouth-to-mouth artificial respiration, which may be supplemented by the use of a bag-mask respirator, or a manually-triggered oxygen supply capable of delivering 1 liter/second or more. If the victim is breathing, oxygen may be administered from a demand-type or continuous-flow inhalator, and preferably with a physician's advice. Contact a physician immediately.

VIII. INDUSTRIAL HYGIENE PRACTICES

1. General Practices

Food should be kept in clean designated areas. Before eating or consuming beverages, face and hands should be thoroughly washed.

2. Inhalation

This compound should be handled in well-ventilated areas in order to minimize the potential exposure to combustion products. Control of these inhalation exposures can be achieved through the use of a cartridge-type NIOSH-MESA approved respirator.

3. Skin Contact

Dermal exposure must be avoided through the use of fire retardant clothing. During sampling, disconnecting lines or opening connections, additional protective outerwear including full face shield, impervious gloves, aluminized Nomex coat, a hard hat and chemical safety goggles should also be worn.

4. Eye Contact

During sampling, disconnecting lines or opening connections, chemical safety goggles and a full face shield should be worn.

IX. HANDLING SPILLS

Block off source of spill, extinguish fire with extinguishing agent—see Section V. Caution—Reignition may occur. If fire cannot be controlled with extinguishing agent, keep a safe distance, protect adjacent property and allow product to burn until consumed.

X. CORROSIVITY TO MATERIALS OF CONSTRUCTION

The product is not corrosive under inert conditions to metals commonly used in construction. Some plastics and elastomers may be attacked. Texas Alkyls, Inc. (713) 479-8411 or Stauffer Chemical Company, Specialty Chemical Division (203) 222-3000 should be contacted for specific recommendations.

XI. STORAGE REQUIREMENTS

Exercise due caution to prevent damage or leakage of container. The product should be stored under an inert atmosphere and away from heat. See Sections III and X.

XII. DISPOSAL OF UNUSED MATERIAL

Combustion of the material by controlling feed of air and product is a suitable disposal procedure. The products from complete combustion are carbon dioxide, water and zinc oxide. Alternately, disposal can be achieved by diluting the product with hydrocarbon (heptane, etc.) to less than 3 weight percent metal alkyl concentration and treating the hydrocarbon solution with water under a nitrogen atmosphere in a vented and agitated container. Allow for the generation of heat and flammable gas when treating with water. The products from hydrolysis are ethane and zinc oxide (hydrated). Conduct water treatment in the absence of oxygen to avoid possible ignition of flammable material.

XIII. DISPOSAL OF CONTAINERS

Zinc alkyl shipping containers are returnable to Texas Alkyls, Inc., Deer Park, Texas. Return shipments of containers are to be made under DOT regulations.

does not significantly react with cellulose under process conditions. Although cellulose has compounds with loosely held hydrogen ions attached to it, some have hypothesized that the oxidation of these compounds in air binds the hydrogen ions. If there is any reaction with the DEZ, however, it is very slow.

Most common metals used in equipment and construction do not react with DEZ. In general, metal alkyls are not corrosive and the original plants at Texas Alkyls are still in operation. DEZ does, however, degrade many elastomers used in gaskets and seals. Texas Alkyls has developed over the years numerous specifications for gaskets, seals, piping, valves, etc. Other materials being used in the plant that have not been specifed by Texas Alkyls have been tested for compatibility by soaking samples in DEZ at ambient conditions.

There are two critical physical properties of DEZ which are not known that impact the design of the hardware. One of these is the specific heat of DEZ. The specific heat of a material determines the temperature changes that occur when the material is expanded or compressed. DEZ vapor is expanded and compressed a number of times during permeation. To ensure that DEZ does not get too hot during compression, pumping rates and pipe sizes must be specified according to the specific heat of the material. Since this has not yet been determined, the most conservative values, those for nitrogen gas, have been used for design purposes. Early pilot plant tests indicate that DEZ vapor temperatures can be satisfactorily controlled.

Heat transfer properties of DEZ are also not known. These properties are needed for designing the condensers and vaporizer. Heat transfer values for a typical hydrocarbon believed to behave similarly to DEZ were used for design. The actual values for both heat transfer and for specific heat will be determined during testing and incorporated in the full-scale design.

Although the exothermic reactions are well-established, it is difficult to predict what changes in temperature will occur in the books and the chamber during permeation. Heat will be generated in the books from the reactions taking place, and other possible causes. Attempts have been made to model the amount of heat retained by the books, the amount exchanged with the gases, and the amount dissipated by the chamber, however, the results have not agreed with the experimental data from the previous NASA tests.

Design and operating conditions have been developed based on the maximum temperature increase observed in previous tests. Extensive instrumentation, a conservative temperature limit for the system, and the ability to quickly introduce cool nitrogen gas into the chamber should allow an acceptable level of control of temperatures.

Also important is an understanding of the compatibility of various fire-fighting agents and techniques. Obviously, water as an extinguishing agent would not be appropriate for fighting a DEZ fire. DEZ fires are difficult to extinguish, however, reasonably effective techniques for controlling a DEZ fire have been established. Fire associated with small spills can be controlled by spreading dry chemicals, sand, or vermiculite over the spill. This prevents DEZ vapors from coming into contact with the air. However, if the spill is disturbed, the trapped vapors could escape and reignite. If the spill is large, the fire is normally allowed to burn itself out. If a large fire is in an area that threatens other equipment, a fine water mist can be used to dissipate the heat of the fire, thus protecting nearby equipment, storage tanks, etc.

Design for Safety

The Library has put together a competent design team for the second pilot plant. They have retained the full-time service of a chemical engineer (consultant) who is responsible for overseeing the design, construction, and operation of the plant on a day-to-day basis.

The Library has contracted with Texas Alkyls to design, construct, and operate the plant. Texas Alkyls has been manufacturing metal alkyls since 1959, and DEZ for nearly as long. They have developed well-established specifications for materials for construction, hardware, etc.

The actual design and construction of the plant has been subcontracted to S&B Engineering. S&B

Photo credit: Library of Congress

This double-block valve at Texas Alkyls pilot plant is a key element in the safety system. It is controlled by the computerized distributive control system (DCS).

has designed and contructed two other metal alkyl plants for Texas Alkyls.

The principal safety-related design criteria for the second pilot plant, and those which will probably be used for the full-scale plant as well, are:

- use a minimum amount of DEZ, and keep a strict inventory;
- keep DEZ in the system and air out of the system;
- prohibit liquid DEZ or liquid water from getting into the chamber, or from coming into contact with each other anywhere else in the system;
- keep the temperature throughout the system below 80 ° C;
- use a computerized distributive control system (DCS) to operate a series of safety interlocks; and
- design all lines and containment vessels for both high and low pressure and provide proper pressure relief mechanisms.

A minimum amount of DEZ will be in the system at any one time. Only the amount needed to complete one batch treatment plus some reserve to allow for variations in DEZ requirements will be transferred from the liquid DEZ storage tank, located 15 feet from the plant, to a DEZ holding tank inside the plant. The holding tank is separated from all other plant systems by a fire wall. The DEZ is vaporized and recycled continuously during permeation.

To reduce the risk of component or line failures and the subsequent release of DEZ to the atmosphere, well-established specifications developed over the years by Texas Alkyls are used for materials and construction. Wherever possible, reliable (and tested) off-the-shelf pumps, valves, heat exchangers, etc. are used. In cases where hardware may use materials not specified by Texas Alkyls, materials compatibility tests have been run, by exposing the materials to liquid DEZ for a few days and analyzing for deleterious reactions.

The design deficiencies cited in the first pilot plant accident report have been eliminated. Redundancies have been designed into the system to prevent either liquid DEZ or liquid water from getting into the chamber and to prevent water and liquid DEZ from coming into contact with each other anywhere in the system. The design of the chamber was evaluated against a worst case scenario where liquid DEZ comes in contact with liquid water in the chamber. The design was reviewed by two independent consultants to ensure that the chamber could contain the resulting overpressure and safely vent it to the atmosphere.

To ensure temperatures stay below 80 ° C, more instrumentation has been added to monitor temperatures and pressures. The capability to circulate heated or cooled nitrogen gas through the chamber has been added to better regulate book temperatures during processing.

Operation of the pilot plant will be aided by a computerized distributive control system (DCS). The DCS will continuously monitor the entire system and manage a series of interlocks to ensure that all operations are performed in the proper sequence and under accepted conditions. If operations have been performed out of sequence or if conditions in the system are not acceptable, the DCS will not allow the process to proceed. The operator cannot override the DCS without action from the shift supervisor. In an emergency situation, the DCS will safely shut the system down. A backup electrical supply will allow the DCS to safely shut the system down in the event of a power failure. Texas Alkyls has gone as far as requiring a check for thunderstorms which may affect power supplies before initiating the permeation stage of the process.

Should a spill, leak, or over pressure situation arise, measures have been taken to isolate the hazard from personnel and from as much of the plant as possible. Liquid DEZ is kept in one corner of the processing area, behind a fire wall. The floor is sloped to route any spills and fire away from the processing area and other liquid DEZ vessels. Remote handling of the system will keep the operator isolated in a control room behind a fire wall and away from any flares due to DEZ leaks. All lines and containment vessels are equipped with pressure relief valves that will safely vent gases to the outside environment. All pressure relief systems are designed to National Fire Protection Association codes.

Hazard alarms have been placed around the plant to alert the operator to heat, fire, or explosion. Hand-held extinguishers are placed around the plant for both electrical fires and DEZ-related fires. Manually initiated sprinkler systems capable of applying a fine mist of water have been installed throughout the plant to help dissipate the heat from any fire and protect personnel and surrounding equipment. The sprinkler system is not activated automatically, since it may not be the appropriate response. The appropriate fire control action is left to the judgment of the operator. The alarm systems, sprinkler system, and hand-held fire extinguishers have been designed in accordance with accepted National Fire Protection Association codes.

It has also been suggested by the Library's outside safety specialists that (for the full-scale plant) the building and the fire wall separating the chamber room from the control room be designed to withstand an overpressure of 80 to 100 pounds per square foot, in case of explosion.

Operational Safety

The safe operation of the system demands skilled and experienced operators. These operators must be thoroughly trained not only in the operation and logic of the entire system, but also trained in the hazards of DEZ, in general, safety and emergency operations (including fire fighting and first aid), housekeeping, and maintenance. The consequences of a breakdown in operational safety are evident in the first pilot plant accident.

The use of a computerized distributive control system demands that the interaction between man and computer is firmly established. This requires a detailed operating manual that clearly spells out the respective responsibilities of the operator and the computer and extensive hands-on training.

Texas Alkyls brings over 20 years of expertise to the operation of the pilot plant. Texas Alkyls has developed safe and effective operating, inspection, maintenance, housekeeping, and emergency procedures. They have reported only five loss time accidents since 1959. Furthermore, they have reassigned eight of their top operators to work on the deacidification program. These operators have received 12 hours of training on the distributive control system as well as 1½ months of training on the total system during the commissioning of the plant.

Safe operation of the DEZ system also requires detailed operating procedures. The pilot plant operating manual was reviewed by OTA, as well as the Library's outside consultants. In general, the degree of detail was judged to be satisfactory, although it was not yet complete at the time of the review. The manual divides the 3 major steps of the process into 17 smaller, more detailed steps. Each step contained a general description, a detailed set of oeprations, which included the reason for each operation and appropriate precautions, a list of the permissives that must be met before initiating the step, and a list of the various interlocking conditions governing the step. The manual also contained the startup and shutdown procedures and a general description of emergency procedures. There was some concern that the manual may be vague in certain areas, relying too much on the expertise already existing with the Texas Alkyls operators. If this manual serves as the basis for the manual used at the full-scale facility, it must be modified to apply to operation by personnel with less plant experience.

Safety Management and Review

Safety management and review is so important that it must be considered at every stage of process development—design, construction, and operation.

It is advisable, at the beginning of a development program, to setup a distinct safety function within the management of the program. This management would be responsible and accountable for designing and implementing a safety plan. The plan should establish what kind of safety analyses and outside reviews are appropriate; schedule and conduct these anaylses at the appropriate times; document the safety needs and requirements that come out of the analyses; ensure that these needs and requirements are included in the design and specifications of the plant, hardware, and operation manuals; and document the implementation of these needs and requirements in the final construction and installation of equipment.

Analysis is a key element to a successful safety program. There are a variety of safety analyses that have been developed. They all incorporate the same basic principles—identify the hazards associated with the process or plant, determine the various ways these hazards may come about and the consequences of them occuring, and determine the best way to eliminate or reduce the chance or the consequences of them occurring.

The analyses, however, are of no practical use if the results are not carried out. Documentation and verification are critical.

The Library has made safety a distinct function within the management of their program. The consulting project engineer has coordinated both in-house and outside reviews, and has received reports on the results.

The Library, Texas Alkyls, and S&B Engineering conducted an in-house "HAZOP" review. "HAZOP" was developed by DuPont Management Consulting Services to assist in identifying and eliminating or minimizing the risks associated with chemical processes. The review used piping and instrumentation diagrams and examined them line by line. For each line the following questions were asked:

- What happens to the process as a whole if the following deviations occur in this line?
  —Flow—too high, too low, reversed?
  —Pressure—too high, too low?
  —Temperature—too high, too low?
  —Concentration—too high, too low, contaminant?
  —Batch timing—too soon, too late, too short, too long?
  —Utilities—failure?
  —Others—commissioning, maintenance?

Besides examining each line, each major piece of hardware is also reviewed.

If any credible consequences were identified, the process was examined for possible causes (including multiple failures), in the absence of protection. If possible causes were identified, then the effectiveness of the existing protections were reviewed. If the existing protections were considered inadequate, assignments were made to study the problem further and take appropriate action. This was done before specifications, layouts, and procedures are finalized to allow flexibility in solving problems.

The results of this review have been tabulated, but the documentation could be improved. A number of possible events (or causes) are identified. Associated with each event is a general description of the existing protection, the necessary actions to be taken and those responsible for taking the action. The actions to be taken were written in very general terms, for example:

- action—DC logic (the distributive control system), or
- action—define operating procedures.

Before testing began, some of those who participated in the HAZOP exercise reviewed the various action items to ensure they were accomplished satisfactorily.

Outside Reviews

The Library has hired six outside consultants to perform independent reviews in the following areas: plant operability, pressure vessel design; vacuum design; fire safety; and a worst case scenario. The consultants reviewed the designs for the pilot plant and those that exist for the commercial plant, before any hardware orders were placed. Written reports were presented to the Library. Any differences in opinion were discussed and resolved by consensus, although there is no documentation of this. However, the Library did perform a second outside safety review after the final construction of the pilot plant to verify that the various safety requirements and recommendations were implemented. The review was conducted by the same six outside consultants. Those with comments were invited back a second time to review the implementation of their recommendations.

SAFETY OF FULL-SCALE PLANT

Although a successful pilot plant program can demonstrate the safety of the DEZ system, it cannot assure it. The safety of a full-scale plant will depend on carrying forward all of the efforts and expertise that have gone into the pilot plant program. In addition, the full-scale plant will introduce public safety concerns.

Transportation Issues

The transportation of liquid DEZ to the full-scale plant will present a new set of risks to public safety. The principal hazard is fire. Leaky valves, a common event in the transport and handling of tanks, could cause DEZ vapors or liquid to be released and ignited. There is also the threat of explosion or rupture if the DEZ inside the tank disassociates. A firey truck accident, also not uncommon, could damage the relief valve and expose the tank to very high temperatures. If gases evolved as a result of rapid disassociation cannot be vented safely or quickly enough, an explosion could occur.

During the course of a year, Texas Alkyls will be trucking 15 to 20, 430-gallon tanks of neat liquid DEZ from their facility in Houston to the full-scale plant site. These will be individual shipments, since the storage of DEZ at the plant site will be kept to a minimum.

The 430-gallon tank will actually contain a nominal 390 gallons of DEZ, or 3,900 pounds. The tanks are standard portable steel tanks, constructed in accordance with DOT regulations (DOT CFR 178.245). They are designed to contain pressures up to 200 psig. The DEZ will be shipped under low pressure. The tank is fitted with a 45-psig relief valve. The tank has a frame around it to facilitate handling.

Texas Alkyls normally ships its DEZ diluted in hexane. Although it is still pyrophoric, the hexane acts as a heat sink, keeping the DEZ below its disassociation temperature. However, because it will be shipping neat DEZ, Texas Alkyls has taken the added precaution of insulating the tank with 4 inches of calcium silicate, and wrapping it in a stainless steel shield.

Photo credit: Library of Congress

430-gallon DEZ storage tanks at Texas Alkyls

The insulated tank was designed with the help of Stauffer Chemicals Research. The design criteria was to limit the temperature rise of the DEZ in the tank to less than 4° C when exposed to a standard DOT bonfire test. The standard DOT bonfire test exposes objects to a temperature of 870° C for ½ hour. A small test cylinder insulated with calcium silicate was subjected to the bonfire test. The cylinder survived the test, the DEZ temperature inside the tank remained virtually unchanged and the paint underneath the insulation showed no signs of being affected by the heat. A similar uninsulated cylinder of propane was tested along side the DEZ cylinder and exploded. Calculations indicated that the 430-gallon tank would require 2 inches of insulation, 4 inches were added as an additional safety factor.

Incidents Involving the Transportation of DEZ

All incidents associated with the transportation of hazardous materials must be reported to DOT. Since 1979, no incidents involving DEZ have been reported. There have been five incidents involving metal alkyls. All involved relatively small volumes. All were fire-related, resulting from faulty valves or valve connections. No injuries were reported; losses totaling about $11,000 were attributed to the incidents.

These incidents apparently involve secondary shipments of metal alkyls. There are no reports that Texas Alkyls has had any incident involving the transportation of its products. They ship their products in sizes ranging from one-liter vessels to railroad tank cars that can hold about 30,000 gallons.

Shipping Plans

The details concerning who and how DEZ will be shipped to the full-scale plant have not been developed. Texas Alkyls contracts a commercial carrier to ship their products. Shipments are normally made in an enclosed van. Normally, Texas Alkyls only provides training to tank truck drivers. They are given a demonstration of what a pyrophoric fire is like, shown a film on the safe handling of DEZ, and instructions on how to deal with local officials in the case of an accident. If considered useful, this training could also be made available to those enclosed van drivers shipping DEZ to the full-scale plant.

During the testing at NASA-Goddard, the Library made preliminary contact with the fire marshalls at Fort Detrick and Frederick because of the plans to locate the full-scale plant at the Fort. Discussions on a safe route from the interstate to the site and fire control techniques were discussed. No formal plans were developed. The Library also approached the Frederick City Council, where the safety of the proposed shipments was debated. These contacts were suspended after the NASA-Goddard accident. If the Library locates the plant at Fort Detrick, the Library intends to revive these discussions sometime in 1989, possibly through the Army Corps of Engineers.

Other Safety Issues Related to the Full-Scale Operation

The decisions as to who will finally be responsible for designing, constructing, managing, and operating the full-scale plant must still be made. From a safety point of view it is imperative that the effort that went into the Texas Alkyls' pilot plant be carried forward completely to the full-scale plant.

It is important that the contractor for the construction of the full-scale plant establish, as early as possible, effective communication with Texas Alkyls and S&B Engineering, who will have acquired the most experience with the process. It is critical that the expertise of Texas Alkyls is transferred completely to the full-scale operation. It is possible that the contract will go to Texas Alkyls.

RISKS

The transportation and use of DEZ poses risks to workers, the public, the plant, and books. These are discussed briefly in the following section.

Risk to Workers

Leaks or spills during operation pose a minimal risk to the worker if safe operations are followed. Operation is remote and the operator sits behind a fire wall. Liquid DEZ is located in the far corner of the plant. The fire control panel used to operate the automatic sprinkler system would be located some distance away from the plant.

During a fire the risk is higher. The operator must decide whether to use the sprinkler system or not. There is an opportunity for an error in judgment. The fire or the intensity of heat can cause injury if the choice has been made to control the fire manually. Proper clothing and breathing devices as well as fire-fighting devices are needed.

The greatest risk to workers occurs during maintenance. Detailed maintenance procedures and tests are needed to reduce the chance of burns. Proper clothing and breathing devices (for enclosed spaces) are needed, and work should be done in teams. The only injury recorded during the development of the DEZ process was a worker at the G.E. test facility that burned his arm when some DEZ mixture dripped on his skin from piping that he was cleaning. The injury was minor, however, and did not require hospitalization.

There is some risk of injury or asphyxiation if a person enters the chamber when the door to the chamber is opened, since this is also a manual operation.

Proper strengthening of walls, etc. should reduce the risks associated with explosion for any enclosed spaces.

Risk to Public

For the full-scale plant, the public is at some risk due to the transportation of DEZ from Houston. Truck accidents are the most frequent incident involving the release of hazardous materials.[2] Furthermore, the tipping or loss of portable tanks during transit are a common mode of accident. Nevertheless, fire during transit would be localized and would not expose a large number of people to the hazard. A more complete transportation risk assessment could be included in the environmental assessment yet to be completed for the full-scale plant.

Risk to Plant

The plant is at greatest risk. Fire due to leaks or spills are inevitable, even if the chances are kept low by proper inspection and maintenance. The types of fire that can be expected will be short in duration but very hot and could cause extensive damage. Damage can be controlled by keeping the fire isolated and cool with an appropriately designed sprinkler system. The chance of explosion is more remote than fire, but the consequences could be much greater.

Risk to Books

The books remain relatively safe. Fire in the chamber is a very remote possibility, given the redundancy in design. Excess zinc oxide deposition, although not necessarily harmful, may create visual problems. Wear and tear from book handling may also cause damage.

DISCUSSION

DEZ is a hazardous substance. Any system using DEZ is susceptible to fire and explosion. However, with proper design and operation, these hazards can be managed.

The second pilot plant has been built to good chemical process engineering standards with careful attention to safety. OTA finds these efforts adequate, but the pilot plant tests during 1988 are needed to demonstrate all safety aspects. As of February 1988, four initial commissioning runs of the pilot plant have been completed in a safe manner and without incident.

The full-scale plant will need equal or greater engineering attention. Scale-up design will need to consider some additional engineering problems. Safety practices will need to consider problems related to a new site, new plant management, new operators, and a new community setting.

OTA has qualitatively assessed the risks and feels the greatest risk is damage to the plant itself. The greatest human risk is to plant workers during initial hookup of the DEZ storage tank, maintenance, or fire-fighting.

There is a marginal risk to the public as a result of shipping DEZ. The Library must take extra precaution to analyze that risk and work with the local community in minimizing those risks.

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[2] U.S. Congress, Office of Technology Assessment, *Transportation of Hazardous Materials*, OTA-SET-304 (Washington, DC: U.S. Government Printing Office, July 1986).

Chapter 6

Health and Environmental Effects

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Chapter 6

Health and Environmental Effects

INTRODUCTION

As with any new process, there is a need to consider the human health and environmental impacts of DEZ treatment of large quantities of books and papers. The Library of Congress has begun a number of studies and intends to do further work prior to building a full-scale treatment plant. This chapter summarizes information about zinc, the health effects of zinc and zinc oxide, the Library risk assessment, and environmental impacts. Concerns about the need for the Library's risk assessment are presented in the *Discussion* section.

The compounds used and produced during the DEZ process are DEZ, water, ethane, and zinc oxide. Although there is currently little evidence to indicate that any of these compounds produce serious health effects, the Library is evaluating the risks the process may pose to workers, librarians, and library users. The Library's effort focuses on zinc oxide, which will be present as particles in the treated books and as dust in the work environment. Of particular concern is the inhalation of these zinc oxide particles. The Library also plans to determine whether any intermediate compounds are formed during the process that would warrant toxicological investigation.

The biological contribution and health effects of zinc and zinc compounds have been studied for many years. Most of the literature relating to inhalation have focused on the effect acute or subchronic exposures have on respiratory function and illness. There have been no tests studying the carcinogenic, teratogenic (birth defects), or reproductive effects of chronic zinc oxide inhalation. Therefore, the Library, with the help of two consulting toxicologists, has designed an animal study to investigate these effects after chronic exposures to the zinc oxide produced by the DEZ process. The results of these animal studies will be combined with exposure measurements at the plant site and at the Library to provide a complete risk assessment.

The other compounds associated with the process are not expected to pose any serious health problems. Ethane is considered to be a relatively benign compound. It is not considered carcinogenic or mutagenic. It is, however, governed by the OSHA limits on hydrocarbons, and can cause asphyxiation in closed quarters.

DEZ is not considered to be a toxicological hazard, either. Its pyrophoric nature precludes exposure. However, dilute liquid mixtures of DEZ can remain stable in air and cause severe burns if it comes in contact with the eyes or skin. (See *Risk to Workers* in previous chapter.) The Library, in an effort to test the toxicity of dilute gaseous mixtures of DEZ, exposed rats to hexane gas containing 20 percent DEZ by weight. The tests were inconclusive. Hexane itself is toxic, and rats exposed just to hexane demonstrated similar behavior as those exposed to the hexane-DEZ mixture. Autopsies showed no indication of growths or irritation in either case. Unless there is any indication that exposure to dilute concentrations of DEZ is a possibility, DEZ should not be a toxicological problem.

There have been two recent reviews of the literature on zinc and zinc oxide. The EPA Office of Health and Environmental Assessment reviewed the literature in 1987 in an effort to assist the Office of Air Quality Planning determine whether these substances needed to be regulated as hazardous air pollutants.[1] They concluded that no regulations were needed. The literature was also reviewed by Leonard et al. in 1986.[2] These two reviews provided most of the following information.

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[1] Office of Health and Environmental Assessment, U.S. Environmental Protection Agency, *Summary Review of Health Effects Associated with Zinc and Zinc Oxide: Health Issue Assessment*; August 1987.

[2] A. Leonard, G.B. Gerber, and F. Leonard, "Mutagenicity, Carcinogenicity and Teratogenicity of Zinc," *Mutation Research* **168**: 343-353, 1986.

ZINC

Zinc is an important trace element in all living organisms and in all tissues. It is found in the blood, kidney, pancreas, liver, prostrate, skin, bone, and eye. More than 20 zinc-containing proteins have been identified. These proteins have both structural and functional roles. Zinc enzymes assist in the synthesis of nucleic acids. Zinc also intervenes in a number of physiological functions as well, including various immune responses, the metabolism of hormones, and the stabilization of DNA's double helix. Zinc can also displace other metals. In the case of cadmium, mercury, and lead, the displacement is beneficial. In the case of iron and copper, the displacement has adverse effects.

Table 14.—Zinc Concentrations in the Environment

Soil	10 to 300 µg/kg
Fresh water (unpolluted)	Less than 10 µg/L
Surface water (polluted)	As high as 21 mg/L
Air (around zinc smelters)	Less than 1 $\mu g/m^3$ to 15 $\mu g/m^3$
Air (around certain work sites)	As high as 18 $\mu g/m^3$

SOURCE: Environmental Protection Agency, 1987.

Zinc is naturally found in small concentrations in the environment (see table 14). There are many manmade sources of zinc. These include metal mining, smelting, the production of zinc oxide and the manufacture of products containing zinc oxide, and the burning of refuse. Zinc is used for galvanizing steel and in the production of rubber; and zinc oxide is used in pigments and in skin ointments, astringents, and antiseptics. Zinc oxide is also used to coat Xerox papers and thus is present in many office environments.

The zinc content of the average daily diet ranges from 8 to 18 mg/kg. Most of this is from food and drink. Intake through the skin or inhalation is minimal. The daily recommended allowance for adults is 15 mg/day.

HEALTH EFFECTS OF ZINC AND ZINC OXIDE

Toxicity

There are no adverse effects associated with dermal exposures to zinc or zinc oxide. In fact, there are many zinc compounds used for medicinal purposes, including zinc ointments for the healing of wounds. Zinc compounds are found in baby powders. The Library conducted earlier toxicology tests on rabbits, exposing them to papers treated by the DEZ process. The results indicated that there was no dermal toxicity.

Excessive or chronic oral ingestion of zinc can cause some health effects. Long-term feeding of zinc salts to rodents retarded growth, and led to anemia and metabolic effects. Excessive ingestion can lead to anemia due to the displacement of iron. There was some incidence of anemia attributed to zinc ingestion in children who played with zinc cast toys in alkaline bath waters. The effect can be reversed with the consumption of iron. Ingestion of zinc in excess of 400 ppm is known to cause gastrointestinal distress, including nausea and diarrhea. There have been recorded many incidences of people experiencing these effects after consuming food or drink from galvanized containers. Long-term ingestion of excessive amount of zinc or zinc oxide can cause immunological and cardiovascular effects. However, there is no evidence that chronic ingestion of zinc is poisonous.

The acute inhalation of zinc or zinc oxide particles, on the order of 0.15 µm in size, can produce adverse health effects known as "metal fume fever." It is normally associated with welding and other zinc industrial environments. The symptoms include fever, nausea, headaches, and dryness of the mouth and throat. The effects are reversible in 24 to 48 hours. OSHA has set an acceptable exposure level at 5 mg/m^3 for an 8-hour workday. Subchronic exposure to zinc oxide fumes, even somewhat below the OSHA level may cause gastrointestinal damage such as peptic ulcers and liver dysfunction and increased respiratory illness and infection. Whether these effects can be expected from working around the treated books or during plant operation, depends on the particle size and the amount of exposure. This will be discussed in the section on exposure.

Mutagenicity, Carcinogenicity, Teratogenicity

Zinc is not considered mutagenic. There is some evidence that zinc acetate may cause chromosomal aberrations in certain cells, but the cells that were studied were not those normally used for studying chromosomal damage.

There is no clinical evidence that indicates ingesting or inhaling zinc or zinc oxide causes tumors. Examination of a variety of tumors show no correlation with zinc concentrations in the tissue. However, there have been no valid studies from which to evaluate zinc's carcinogenicity. Tumors have been caused by repeatedly injecting the testicles of birds and rodents with zinc salts. Zinc metal powder injected into the trachea of animals has also produced tumors. In all of these cases, the tumors were located at the site of injection. Injection is not considered a valid exposure route and unless it causes tumors away from the site of injection, it is not considered a valid indication a substance's carcinogenicity.

Because of zinc's role in DNA synthesis and cell growth, zinc has been associated with promoting the growth of certain tumors. In other cases, zinc has inhibited tumor growth.

Zinc is not considered to be teratogenic. In fact, zinc deficiency is known to be a major cause of birth defects, and zinc can reverse the teratogenic effects of cadmium. For this reason zinc supplements have been given to pregnant women. However, there have not been any teratogenic studies related to the chronic inhalation of zinc oxide.

Excessive zinc has adversely affected fertility and pregnancy in rats. The effect may or may not be similar in humans. Normal levels of zinc do not appear to be a problem. Pregnant women who have been given zinc supplements, up to 81 mg/day during their final 3 months of pregnancy, have shown no adverse effects.

LIBRARY'S RISK ASSESSMENT

Animal Study

The Library has designed an extensive animal test to study what effects the acute (14 days), sub-chronic (91 days), and chronic (2 years) inhalation of zinc oxide particles may have on pulmonary function and male and female reproductive capabilities, and to determine the carcinogenicity and teratogenicity of chronic inhalation of zinc oxide particles. The study will expose rats to acute, sub-chronic, and chronic inhalation of zinc oxide particles at various concentrations in air, including a zero percent zinc oxide control. Clinical and gross pathologies will be performed on all specimens and organs. Pulmonary physiology will be examined in some specimens and pathology of the respiratory track will be performed on all specimens. An examination of sperm morphology and vaginal cytology will also be performed on specimens in the sub-chronic and chronic studies. Some specimens from the sub-chronic exposures will be mated to study the reproductive and teratogenic effects.

All tests will be performed in accordance with the National Toxicological Program guidelines for good laboratory practice.

Exposure Study

As part of its risk assessment, the Library is determining the particle size and levels of exposure that can be expected for library users, librarians, and process workers. Particle size will determine how deep the particles may go into the lung (e.g., respirability). Particle size v. respirability is given in table 15.

Library users can be expected to be exposed to zinc oxide by leafing through a book. Two methods were used to determine the amount of zinc oxide to which a user may be exposed. One method was to vacuum loose zinc oxide off randomly selected pages of treated books. The other method mechanically leafed through books and sampled the air 5 inches above the pages.

Table 15.—Particle Size v. Respirability

Particle size (μm)	10	5	3.5	2.5	2
Percent respirable	0	25	50	75	100

SOURCE: Northrup Services Inc., "Evaluation of Diethylzinc-Treated Paper: Particulate Emissions," Final Report to the Library of Congress, August 1985.

Librarian exposure will be determined by measuring the ambient air concentration of zinc oxide in a simulated stack of treated books.

Worker exposure will be determined by taking air samples at the chamber door, when the door is opened and closed.

Results from the user exposure study indicated that the particle or aggregated particle size averaged 0.6 to 1.5 μm by 0.4 to 1.0 μm. Particles of this size are respirable, but 90 percent of those measured were above the 0.15 μm particle size related to metal fume fever.[3] In addition, the maximum airborne concentration, 5 inches above a mechanically leafed book, was 0.06 $\mu g/m^3$, well below the OSHA acceptable limit. The concentration of particles taken from the vacuumed pages ranged from 9 million particles per cubic meter to 45 million. This is also below what would be considered a toxic concentration of about 1 billion particles per cubic meter.[4] Therefore, the exposure of Library patrons to the zinc oxide in treated books should not result in any known health effects. Whether or not these concentrations will cause other health effects depends on the results and interpretation of the animal study results.

The exposures of Library workers and plant workers to zinc oxide have not yet been measured at the time of this report.

ENVIRONMENTAL IMPACT

In 1984 the Library prepared an initial environmental assessment of a proposed DEZ plant at Fort Detrick. The purpose of the assessment was to determine to what extent the siting, construction, and operation of the plant would impact the local surroundings and community. The assessment, based on the scaled-up design of the first Goddard pilot plant, determined there would be no significant impact. The assessment was reviewed and approved by Fort Detrick personnel, but the accident at Goddard halted the process before it was presented to the Army Corps of Engineers and the community for review.

The Library intends to initiate a new environmental assessment after the full-scale plant design is completed and a site has been selected. If the plant remains at Fort Detrick, as originally planned, a more comprehensive assessment than the first will be required. If another site is chosen, a new, comprehensive assessment will probably be necessary. Any ethane emissions will need to meet local air pollution regulations. Other impacts will need to be reviewed and evaluated for a new site. The Library must allow adequate time for environmental assessment to avoid delaying the construction of the plant.

DISCUSSION

OTA, with the assistance of consulting toxicologists, met with the Library's consultants, to review the studies both completed and planned. There was a general consensus that the search of the existing literature was thorough, and that there was a lack of studies directed at the effects of chronic inhalation. The planned animal study designed by the Library's consultants was also considered to be thorough and followed the accepted protocols. There were, however, a couple of concerns expressed by OTA consultants.

There was some concern that the rat may not be an appropriate model of the human respiratory system. Rats have a greater clearance, i.e., can better remove particles from their lungs, than can humans. The amount of zinc oxide actually reaching the rats lung (i.e., the actual dose) may be proportionately far less than what would be expected to reach a human's lung. It was suggested that a prestudy test, measuring the clearance of various models including the rat, could determine the most appropriate model or at least determine the actual amount of zinc oxide getting into the rats lungs.

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[3] Northrup Environmental Sciences, Triangle Park, NC, *Evaluation of Diethyl Zinc-Treated Paper: Particulate Emissions*, a report prepared for the Library of Congress, August 1985, p. 4-1.

[4] Ibid., p. 4-2.

There are some practical limitations to using other animals too. The life span of other laboratory animals like rabbits or cats would make the chronic exposures more expensive. Some animals' lungs, such as the mouse's lung, are not sensitive enough for respiratory studies. Also there is a good inhalation database for rats. The Library analyzed this problem and concluded that it would be acceptable to use the rat model.

There was also some question as to the need for the Library to perform evaluations on the chronic effects of zinc oxide inhalation if the levels of exposure are below those experienced in the acute and sub-chronic literature. Although there is no evidence to suggest that low levels of zinc oxide cause chronic effects or is carcinogenic, this is not sufficient to say that there are no chronic effects or that zinc oxide is not carcinogenic. Therefore, the Library and its consultants contend that it is in the Library's interest to perform a large-scale investigation into this area. It is not clear, however, whether a single study can resolve the issue. Therefore, there is a question as to how much time and effort the Library should spend in generating information that may have only a marginal value. It was suggested by one of OTA's consultants that the Library perform the exposure analysis and determine whether the levels are comparable to or below those already studied in the literature. If they are greater, then the rest of the study should be conducted. If they are below, then an extensive review of the literature and the exposure study should suffice.

Part II

Comparison of Alternatives for Book Preservation and Deacidification

Chapter 7

Alternatives

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Chapter 7

Alternatives

INTRODUCTION

Part II of this report discusses possible alternatives to the Library's proposed deacidification system. The main alternatives that are described are the Wei T'o, Bookkeeper (Koppers), and Interleaf Vapor Phase Deacidification processes. Advantages and disadvantages of these three main alternatives to the Library's DEZ process and an ideal deacidification system are discussed along with the effectiveness; costs; and impacts on safety, health, and the environment.[1] Other processes that OTA obtained information on, but was unable to thoroughly analyze are identified in this section of the report. The potential for increasing the use of acid-free paper and what effect, if any, this might have on the Library's program, is also discussed.

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[1] Separate contractor's report to OTA comparing the effectiveness of these processes is also available from OTA upon request: David N.S. Hon, "An Evaluation of Mass Deacidification Processes for Book Preservation and a Comparison of Their Chemical Characteristics and Effectiveness," Clemson, SC, November 1987.

ALTERNATIVE PROCESSES

Wei T'o

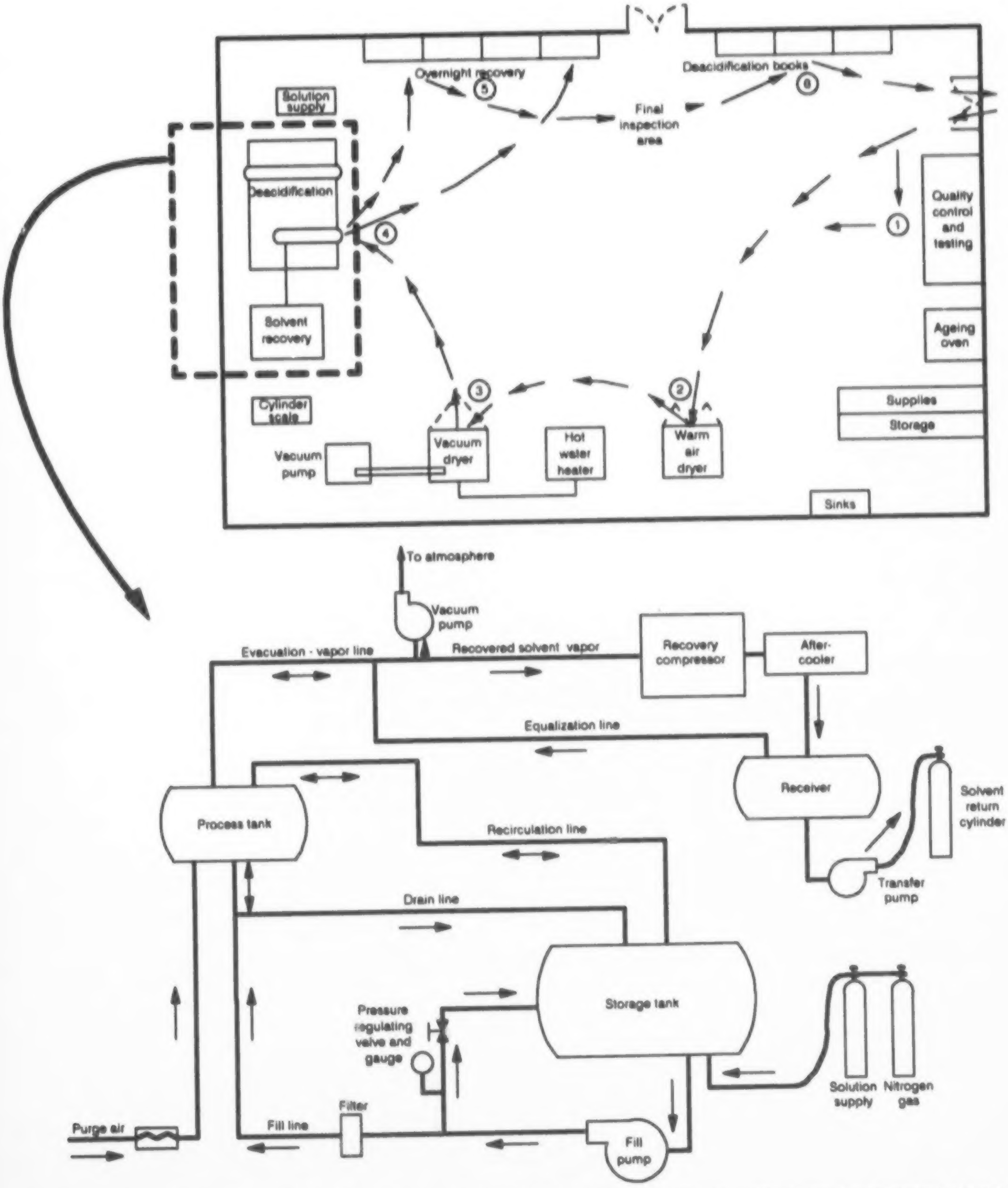
The mass deacidificiation process developed by Wei T'o Associates is a nonaqueous liquid process that uses the same basic chemistry as the manual Wei T'o processes currently in use in many libraries. A mass deacidification pilot plant was built for the Canadian National Library and National Archives in 1979. The plant was designed to treat 30 books at a time. Since 1981, the Canadian Library and Archives have been operating the system on a semi-production scale basis, treating about 120 to 150 books per 8-hour day. The Canadian Library has no immediate plans to scale-up the process. Wei T'o has a preliminary design and cost assessment for a system that would double the batch size and optimize the system's throughput.

The Wei T'o process uses methoxy magnesium methyl carbonate dissolved in methanol, and mixed with Freon 12 and Freon 113. These freons are liquid gases, normally used as refrigerants, that allow the methoxy magnesium methyl carbonate/ methanol solution to penetrate into the paper. Books are immersed in the solution and the methoxy magnesium methyl carbonate reacts with moisture in the books, theoretically forming magnesium carbonate, magnesium hydroxide, and magnesium oxide. These compounds will react with acids in the paper to form stable, neutral salts. Excess magnesium carbonate, hydroxide, and oxide will join together to form a mixture (called basic magnesium carbonate) that acts as the alkaline buffer.

The system in place at the Canadian Library includes a warm air drier, a vacuum drier, and the processing unit, which includes the processing chamber, a storage tank, and a recovery tank and condenser (see figure 22). The storage tank holds the Wei T'o solution under pressure. To begin treatment, the solution is pumped through a filter to remove impurities such as paper fragments loosened from books into the processing chamber. After treatment, the solution flows back into the storage tank for reuse. Vapors from the chamber are evacuated and passed through a condenser and fed into the receiving tank, which can then be sent back to Wei T'o for reprocessing.

Selected books are placed in metal crates and dried in warm air to remove a large amount of moisture. Before being treated, the books are placed in first one and then a second vacuum drier to reduce the books' moisture content to 0.5 percent. In the second vacuum drier the books are heated

Figure 22.—Wei T'o Process [Steps in Sequence 0]


Solution supply
Deacidification
Solvent recovery
Cylinder scale
Vacuum pump
Vacuum dryer
Hot water heater
Warm air dryer
Sinks
Overnight recovery
⑤
Final inspection area
Deacidification books
⑥
①
Quality control and testing
Ageing oven
Supplies
Storage
②
③
④
To atmosphere
Vacuum pump
Evacuation - vapor line
Recovered solvent vapor
Recovery compressor
After-cooler
Equalization line
Receiver
Solvent return cylinder
Transfer pump
Process tank
Recirculation line
Drain line
Storage tank
Pressure regulating valve and gauge
Solution supply
Nitrogen gas
Purge air
Fill line
Filter
Fill pump

SOURCE: R.D. Smith, "Mass Deacidification at the Public Archives of Canada," *Conservation of Library and Archival Materials and Graphic Arts*; Guy Petherbrige (ed.) (London: Butterworth's, 1987).

to about 100° C and held there overnight at a pressure of 0.2 torr. The books must be dry to allow good process control. Total drying time is about 24 hours.

The books are then transferred to the processing chamber. The chamber is bolted closed and a vacuum pump evacuates the air and moisture from the chamber. The books must be treated in a dry environment because the solution will react with excess moisture and turn into a gel. When the chamber has been evacuated, it is backfilled with vapors recycled from the receiving tank, equilibrating the process chamber pressure with the storage tank pressure. This is done to avoid any turbulent flow when the solution is fed from the storage tank into the process chamber. The solution is introduced slowly to avoid forming any bubbles that may result in non-uniform impregnation of the books. Once the chamber is filled, it is stabilized for 4 minutes and then more solution is added to increase the pressure in the chamber. The chamber is left under pressure for roughly 40 minutes to allow adequate penetration of the solution into the books' pages.

When the treatment is completed, the solution is drained back into the storage tank. After the chamber has been completely drained, a vacuum pump removes all the excess vapors, routes them through a condenser, and the liquid is stored in the receiving tank. This removes a large fraction of the excess solution and freon left in the books. The chamber is then purged with warm air and opened. The crates are removed and placed in a storage cabinet overnight, where the remaining solution and freon evaporates until the books warm up and regain a portion of their original moisture content. They regain the rest of their moisture slowly after leaving treatment.

The chemical treatment step takes about 1 hour. This includes the time it takes to pull another vacuum on the chamber after the books have been removed to minimize the amount of vapors left in the chamber and eliminate fouling of the chamber. Total cycle time is roughly 26 hours plus the cabinet storage time after treatment. The Canadian plant treats about four to five batches of 30 books each per 8-hour day with two operators for the entire plant or about 42,000 books per year.

Bookkeeper Process

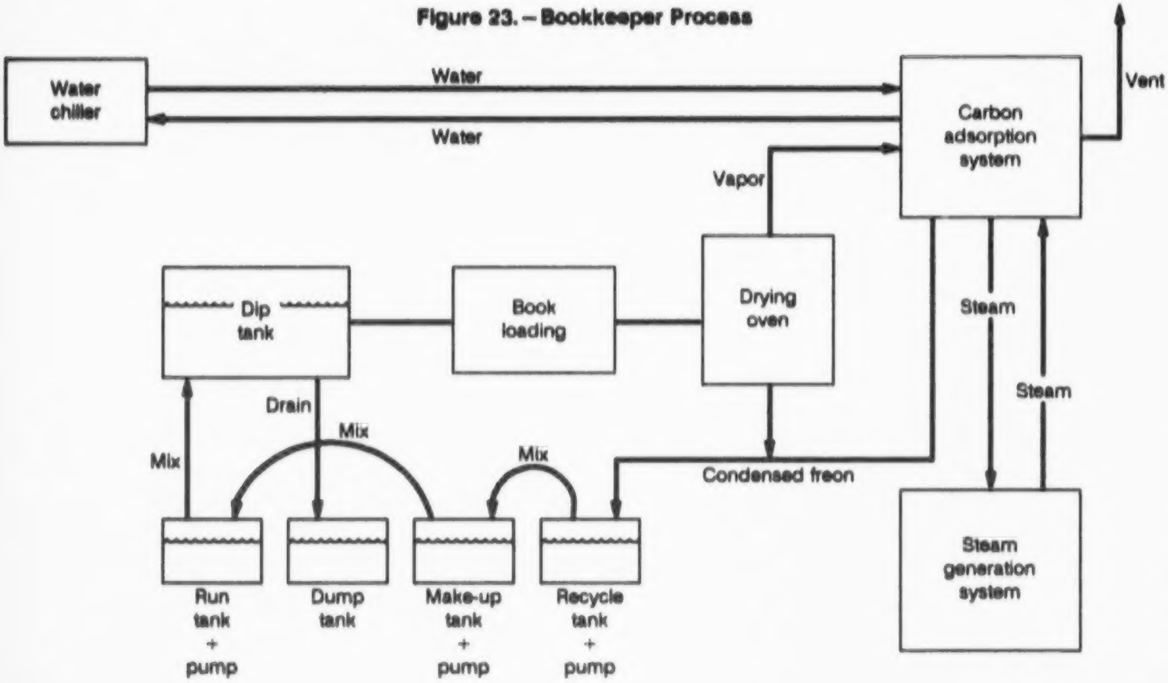
The "Bookkeeper" process is a nonaqueous liquid process that was initially developed by the Koppers Chemical Co. beginning in 1981. Development progressed to a detailed design of a pilot facility capable of treating 100 books per day. An agreement was negotiated between Koppers and The University of California at Berkeley to construct and demonstrate the pilot system at the university. Koppers halted the project, however, after they concluded that the Library of Congress was committed to the DEZ process and that the private library business potential was too limited. Koppers has since sold the patent to Richard Spatz, who recently retired from Koppers. In 1987 Mr. Spatz contracted with Koppers to have the original development team continue work to improve the system under the name "Bookkeeper."

The "Bookkeeper" process uses a suspension of fine (submicron) particles of magnesium oxide dispersed in a fluorocarbon (e.g., Freon 113) and a surfactant. No solvents such as methanol are used. The fluorocarbon carries the particles into the paper and the surfactants keep the particles evenly dispersed in the mixture. The process does not immediately neutralize the acids present in the paper. Rather, when the books are immersed in the mixture, the magnesium oxide particles are implanted into the paper and deacidification occurs later as the acids migrate to and react with the particles over time.

The process is capable of being designed as either a batch or a continuous process. The pilot plant was designed as a batch process and designed to fit in a tractor trailer. It consisted of storage/mixing tanks, a loading area, a treatment tank, and a drier/condenser. (See figure 23.)

Books do not have to be predried in this process. Books (current designs hold three books) are loaded into a fixture that spreads the books open to a specified angle. The fixture is then lowered into the treatment tank and the tank is filled with the mixture. The fixture is then mechanically agitated while the mixture is circulated to ensure complete wetting of the book and its pages. The fixture is designed to close the books before they are removed from the tank. Treatment takes only a few min-

Figure 23.–Bookkeeper Process



SOURCE: Adapted from a Koppers Diagram

utes. The books are then removed from the fixture and placed in an air drier. The vapors from the drier are condensed and recycled. Total process time is 4 to 5 hours.

Experiments are currently being performed that place a book fixture, holding about 10 books, in a processing chamber similar to the kind used in the Wei T'o process. The chamber is then filled with the mixture and the books agitated. After the chamber is drained, it is evacuated by a vacuum pump for about 1 hour to evaporate the majority (about 95 percent) of the mixture remaining in the books. Warm freon vapors are then passed through coils in the chamber and the remaining 5 percent of the mixture remaining in the books after treatment is evaporated under vacuum. In this new development, total cycle time may be about 3 hours.

Interleaf Vapor Phase Deacidification (VPD)

The Interleaf process is a vapor phase deacidification process developed in England by Langwell in the 1960s. The patents to the product have been purchased by B.G. Robertson Laboratories. Interleaf, Inc. of Minneapolis is the sole U.S. distributor.

The VPD process uses cyclohexylamine carbonate crystals that are either impregnated on a sheet of paper or placed in a packet that is then placed between the pages of the books to be deacidified. Cyclohexylamine carbonate is a organic derivative of ammonia and is volatile at room temperature. The crystals release vapors that neutralize acids as they permeate through the pages of the book. Placing the packets takes only a few minutes and complete book deacidification is achieved slowly over several days.

The technique is being used at the Public Records Office in London and the United Nations in Geneva. In this country, Interleaf offers this service to customers that are having books rebound and sells the packets to the general public. The largest deacidification project that Interleaf has done involves the deacidification of 1,200 to 1,500 books from a small law book collection. Books are treated in batches of 100 and placed in boxes for 10 to 12 days and then removed.

ADVANTAGES AND DISADVANTAGES OF THE ALTERNATIVE PROCESSES

It is not possible to make a definitive comparison of the various processes at this time. Data assessing the effectiveness of the processes are limited and those that do exist do not fully assess the processes' effect on paper. Nor have any of the processes been developed enough to allow for an accurate assessment of the potential treatment capacities or costs. However, for DEZ and three major alternatives, OTA has made qualitative comparisons of process effectiveness; capacities and costs; and safety, health, and environmental impacts. The results of these comparisons, against an ideal system, are shown in table 16.

Effectiveness

There is a general lack of meaningful data to compare the effectiveness of the various processes. The effects the various treatments have on the chemical properties and behavior of the various chemical components of paper— including cellulose and its hydroxyl and carbonyl functional groups, hemicellulose, and lignin—have not been given much attention. Data on the effect of treatment on optical properties of paper are also limited. Nor has the stability of treated papers to light, pollution, and other degradation mechanisms been properly evaluated. The effects various treatments have on mechanical properties have received the most attention, but the results that have been reported are not conclusive. The change in the degree of polymerization, which some paper chemists feel is a more definitive measure of a process' effectiveness, has not been measured.

The data that do exist have been generated over a long period of time by the individual developers, on different types of papers, under a variety of test conditions, measuring only a few of the important properties. Ideally, a definitive assessment would require a direct comparison of paper specimens treated by the various processes and tested under identical conditions.

Nevertheless, OTA has made a qualitative comparison of the effectiveness of the various processes (shown in table 16) based on the following criteria:

- the need for preselection (i.e., screening) and predrying before treatment;
- cycle times;
- complexity of the treatment plant;

Table 16.—Comparison of Alternative Mass Deacidification Processes, As of January 1988

Criteria	Ideal	DEZ[a]	Wei T'o	Bookkeeper[b]	VPD[c]
Preselection of books	No	No	Yes	Minimal[d]	Yes
Predrying	None	Yes	Yes	None	None
Impregnation time	Short	Long	Short	Short	Very long
Treatment plant	Simple	Complex	Less complex	Simple	Very simple
Effect on inks and colors	None	None	Some	Minimal[d]	Some
Effect on plastic covers	No	No	Yes	Minimal[d]	Yes
Neutralization	Complete	Complete	Needs verification[e]	Needs verification[e]	Partial
pH of treated paper	7.0-8.5	7.0-7.5	8.5-9.5[e]	8.0-9.0[e] (surface)	5.0-8.7
Alkaline reserve	About 2%	1.5-2.0%	0.7-0.8%[e]	2%[e]	None
Danger to health	None	Risk of fire	Uncertain[f]	Uncertain[f]	Uncertain
Impact on environment	None	Low	Uncertain[g]	Uncertain[g]	Low
Stage of development	—	Operating pilot plant (2 mo.)	Operating pilot plant (7 years)	Lab tested pilot design	Commercial
Cost	—	Moderate to high[h]	Low to moderate[h]	Low[h]	Low[h]

[a] Library of Congress' DEZ process.

[b] "Bookkeeper" submicron particle process.

[c] Langwell vapor phase deacidification process—distributed by Interleaf, Inc.

[d] Based on telephone conversation with Dr. J.J. Kozak of Koppers (Nov. 2, 1987). No independent assessment.

[e] No formal independent analyses have been made. Manufacturer's data indicates complete neutralization under laboratory conditions.

[f] Initial indications are good but no formal assessments have been made.

[g] Some concern about the future regulation of fluorocarbons used in these processes.

[h] Based on OTA analysis and extrapolation of limited cost data furnished by developer of each system.

SOURCE: David Hon, "An Evaluation of Mass Deacidification Processes for Book Preservation and a Comparison of Their Chemical Characteristics and Effectiveness," prepared for OTA, November 1987.

- effect on inks and colors, plastic book covers and other materials;
- completeness of neutralization and pH after treatment;
- amount of alkaline reserve after treatment;
- impacts on health and environment;
- stage of development; and
- cost.

In small-scale tests the DEZ process can, very impressively, neutralize all excess acids in the paper and deposit a uniform alkaline buffer. Deacidification byproducts are neutral and stable. An advantage of the DEZ process over all the others is that the initial deacidification occurs independently of the alkaline buffer deposition. As a result, all papers are left nearly neutral after treatment, no matter what their original acid contents may have been. Furthermore, the amount of alkaline buffer deposited can be controlled to a much greater extent and achieve a greater uniformity within a book. However, the uniformity and completeness of treatment from book to book depends on the flow characteristics of the gases in the chamber and the characteristics of papers in the books. Whether very uniform results can be achieved routinely in a full-scale operation must still be demonstrated.

Based on process tests to date, preselection for the DEZ treatment will probably not be needed. The DEZ treatment appears to be compatible with most other book materials including inks, colors, and pigments. It may cause some loss of brightness in nitrocellulose covers. The problem of excess zinc oxide deposits on book covers can be minimized, but depends on the flow of gases in the chamber. The DEZ treatment may leave a slight odor immediately after treatment.

The zinc oxide buffer could increase paper's sensitivity to photodegradation. This is of concern to the Library and they are planning further tests. Some other long-term effects must also be studied further: such as the effect of DEZ/nitro-cellulose reactions. The Library claims that the DEZ process can extend the life of a book three to five times based on fold endurance of test papers. The data that have been presented to support this have not been presented conclusively for the actual books in the Library's collection. Such an evaluation is planned as part of the quality control program that will be developed and tested at the Texas Alkyls pilot plant.

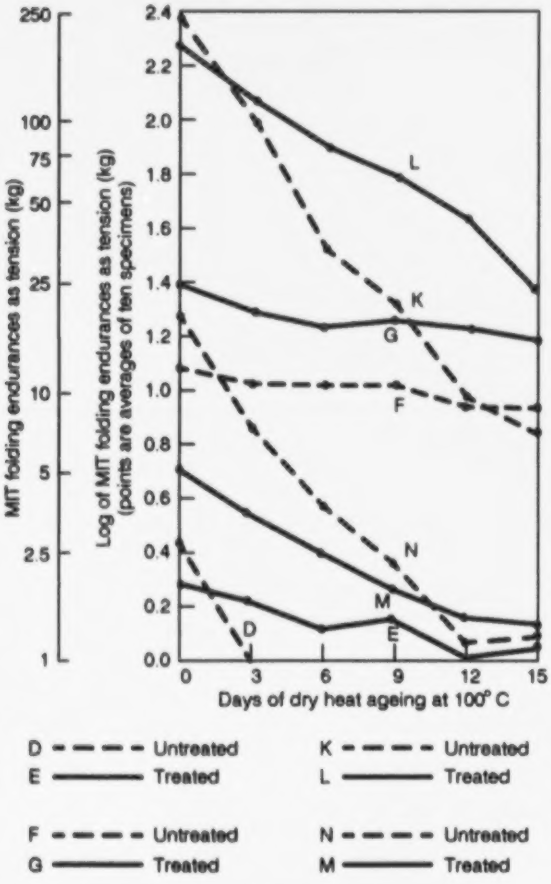
The Wei T'o plant is simpler than the DEZ plant and its chemistry is generally accepted within the preservation community. There is little data, however, on the uniformity of treatment in a mass deacidification system. An examination of one of the books treated when OTA visited the Canadian facility indicated that there were spotty areas where the pages had not been deacidified. Whether this was an isolated case that could be remedied by adjusting the solution concentration or adjusting the process parameters is not known. The alkaline buffer deposited is comparatively small relative to the other processes. The plant also does not appear to have been subjected to a systematic quality control program and no process test results are available.

The Wei T'o process requires pre-inspection of all books about to be treated. The solvents used in the process are known to cause certain colors to transfer and certain inks to run. Experienced operators can determine which books may be affected by simple inspection. With inexperienced operators or when encountering unfamiliar papers and colors, the particular pages must be tested to determine what effect the process may have. Some books cannot be treated at all, others can be treated after placing blank paper between the color pages. Because of its relatively high alkalinity, the Wei T'o process can also cause discoloration after treatment if the paper is exposed to high humidity or water. Certain plastic covers will crack and flake. The reason for this is not known. It may be related to the difference in thermal expansion between the plastic coating and the paper cover. The books cool quickly as the freon and methanol evaporate from the books after treatment. The process does not leave any odor in the books. These various constraints cause rejection of about 20 to 25 percent of the books submitted for treatment.

According to its President, Wei T'o is developing new chemicals for its processes. He claims that new non-alcoholic solvents are being developed to eliminate the problems of color transfer and ink swelling, and that magnesium will be replaced in the deacidifying agent to lower the alkalinity of the treated paper and reduce the problems of discoloration. The status of these new developments is not known.

The long-term effect of the Wei T'o process on various paper properties has not been adequately studied. There is limited published evidence that the mass deacidification system now in use extends the life of books. Some fold endurance test results are shown in figure 24. While improvements in the papers are evident, the description of test conditions and test data is not sufficient for an evaluation of the significance of results.

Figure 24.—Fold Endurance After Aging of Papers Treated by the Wei T'o Process



SOURCE: R D Smith, *Conservation of Library and Archival Materials and Graphic Arts*; "Mass Deacidification at the Public Archives of Canada," Guy Petherbridge (ed) (London: Butterworth's, 1987)

The Bookkeeper process can achieve a uniform deposition of magnesium oxide throughout the pages of a book. Tests of this have been based on x-ray diffraction analysis and scanning electron microscopy. The treatment can also effectively neutralize acids, raising the pH of papers up to 8 or 9. Tests by the developer have shown that fanning the pages of bound volumes is necessary to assure complete treatment and uniform pH values from outer edges to the binding. However, only surface analyses have been performed. Cold extraction pH measurements have not been made. Since total deacidification depends on the original amount of magnesium oxide that gets deposited, it is important to know how much buffer is left to inhibit reacidification. The Bookkeeper developer has done an initial microscopic study of treated paper which shows evidence of some penetration of magnesium oxide particles, but a more extensive test program is needed.[2] If the process proved *not* to completely deacidify the interior of papers, it would be a serious drawback to its use.

The Bookkeeper process is the simplest of the mass deacidification systems and may require the shortest cycle time.

The Bookkeeper process may require little preselection, but the effects of the treatment on paper and other book materials has not yet been adequately studied. Because of the chemicals used in the Bookkeeper process, certain problems associated with color transfer and ink swelling should not be expected. The problem with certain plastic-covered books may present a similar problem for the Bookkeeper process as it does to the Wei T'o process, since it too uses freon that will quickly evaporate after treatment. The process does not leave an odor in the treated books.

As with the other processes the long-term effects of the treatment on the life and other properties of paper have not been adequately studied. Some fold endurance tests have been conducted, and the results are comparable to those for both the DEZ and Wei T'o processes. (See table 17.) Based on this limited data, Bookkeeper claims that the life of a book can be extended two to three times.[3]

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[2] Letter from Richard E. Spatz with enclosures, Dec. 29, 1987.

[3] Kundrot Patent, U.S. Patent No. 4,522,843, Jan. 11, 1985, p. 5.

Table 17.—Accelerated Aging Effects on Fold Endurance of Treated and Un-Treated Papers for the Bookkeeper Process
(aging conditions—70 °C, saturated R.H.)

	Fold endurance (double fold with 0.5 kg)	
Days of exposure	Untreated	Treated
0	1,406	1,390
7	933	1,160
14	619	969
21	410	809
28	272	676

SOURCE: Bookkeeper.

The VPD process is the simplest of all the processes but cannot really be considered a mass deacidification in the same scale as the other three systems. The VPD process does not deposit an alkaline buffer. Protection lasts only as long as the packets continue to give off vapors. The deacidification may not be permanent since the byproducts are volatile and under certain conditions (i.e., humidity and temperature) may revert back to acids. The data relating to the uniformity and completeness of treatment is anecdotal.

Cyclohexylamine carbonate will react with some inks, colors, and plastic covers, and therefore will require preselection before treating. Cyclohexylamine carbonate will also leave an odor in the books. The use of charcoal in the packets reduces the odor only slightly.

Costs

It is difficult to obtain uniform cost estimates for comparing the various processes. Most of the detailed estimates have been independently prepared by the developers of each process and certain major cost categories are not always included. Three types of costs are important: first, the capital cost of a facility to treat a certain number of books; second, facility operating costs per unit time (usually 1 year); finally, per-book costs with assumptions of the total number of books treated per year. These three cost types are presented separately. Because most of the data are available for pilot plant sizes (about 40,000 books per year), cost comparisons will be made only for this capacity.

Capital Costs

OTA has obtained pilot plant capital cost estimates for three processes (DEZ, Wei T'o, and Bookkeeper) from the developers of that process. (See table 18.) Conveniently, roughly similar capacity pilot plants have been designed or built for each.

Operating Costs

To compare operating costs, all important categories for each process must be considered. Since only some of the data are available from developers of each system, OTA made rough estimates of some missing items. Table 19 displays certain operating

Table 18.—Capital Costs of Alternative Systems at Pilot Plant Sizes

Pilot plant	Cost ($ millions)	Books capacity/8-hr. shift
DEZ[a]		50
Design	0.6	
Construction	1.3	
Wei T'o[b] (no design breakout)	0.5	150
Bookkeeper[c] (construction only)	0.4-0.6	100

[a] Based on the actual cost of design and construction for the pilot plant at Texas Alkyls; capacity based on 55-hour cycle time may be modified depending on experiments to be performed during 1988.

[b] Based on actual costs in 1979 reported to OTA by Canadian National Archives. Other information indicates this may also be approximately the replacement cost in 1987.

[c] Based on Bookkeeper design and detailed cost estimate reported to OTA in October 1987. A modification to the design in December 1987 (a closed chamber system) was reported by the manufacturer to have a lower cost.

SOURCE: Office of Technology Assessment, 1988.

Table 19.—Selected Operating Costs for Three Systems at Pilot Plant Sizes
(thousands of dollars per year)

	DEZ[a]	Wei T'o[b]	Bookkeeper[c]
Plant costs	50	100	30
Operating labor	120	80	80
Overhead and administration	30	20	20
Total	200	200	130

[a] Prorated from Library of Congress estimates for full-scale plant.

[b] From Canadian experience.

[c] From Richard Spatz estimates for plant costs and Canadian experience for other costs.

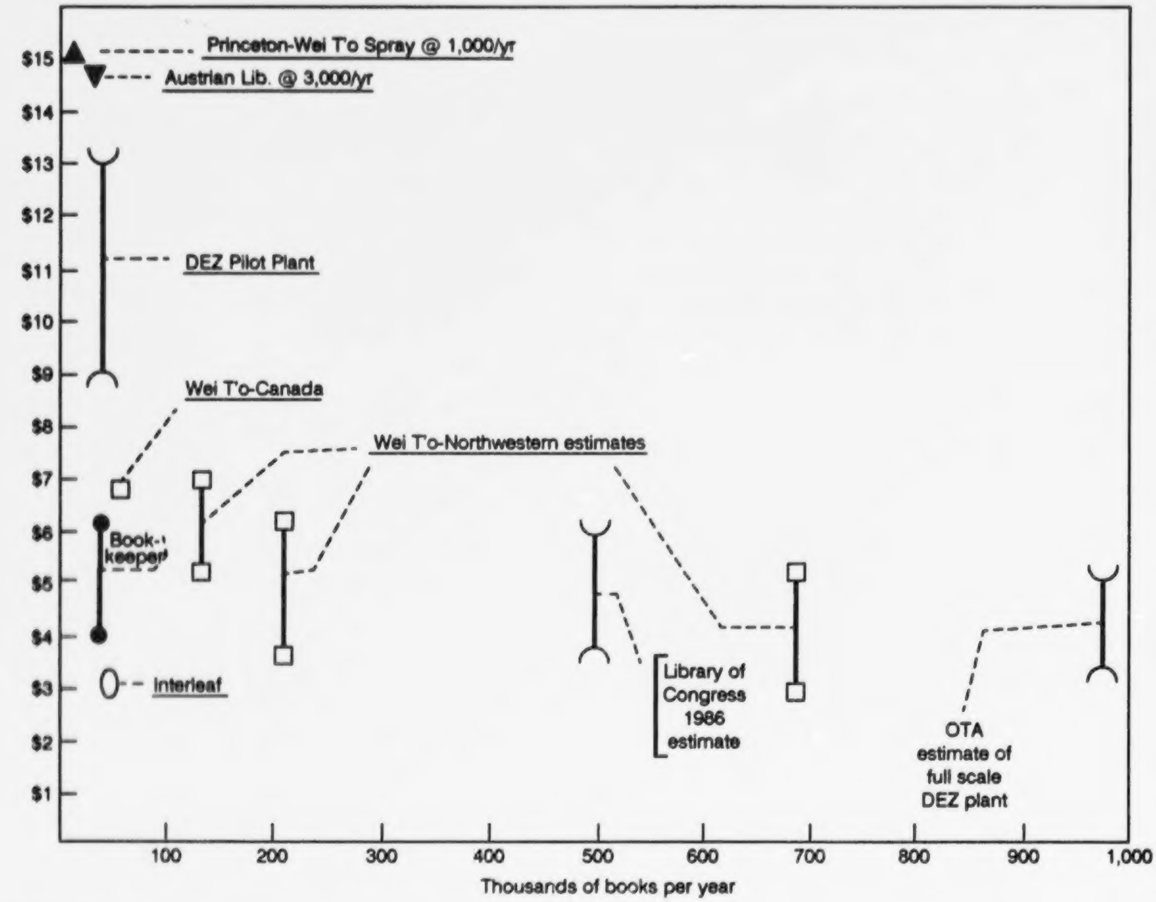
SOURCE: Office of Technology Assessment, 1988.

costs per year for the same pilot plant treatment capacities noted above (assume 40,000 books per year). Operating costs associated with transportation and handling of books to and from a treatment facility are *not* included because these costs can vary significantly depending on the library and the plant location as well as setup.

Per-Book Costs

Figure 25 displays deacidification costs per book from OTA estimates based on a variety of sources. OTA tried to make all costs comparable by adding similar figures for categories not supplied by others. Those costs based upon some operating experience are shown as single values; those based upon projections as ± 20-percent range. It is clear that there are a wide range of costs for the various processes. For the 40,000 book per year pilot plant size, present indications are that the DEZ process is by far the highest cost followed by Wei-To, Bookkeeper, and Interleaf (VPD).[4] Further design, development and testing could change these costs—especially for DEZ and Bookkeeper. The much larger plants, of course, are more uncertain for final costs. Even with this uncertainty, it does ap-

Figure 25.—Estimates of Per-Book Costs for Deacidification by Various Processes, 1987



SOURCE: Office of Technology Assessment, 1988.

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[4] The cost for the VPD process is based on information from the manufacturer of a typical charge he has made in the past for treating a few thousand books at his facility.

pear that the DEZ process will remain the highest cost alternative.

Safety, Health, and Environmental Impact

The DEZ process does pose safety risks to the plant worker and the public. The reactivity and instability of DEZ expose the workers and the public to potential fire. The impact on health is not expected to be serious. The Library has performed a lengthy review of the health effects literature for zinc oxide and has performed a number of toxicological tests. It is also about to perform an extensive animal study to assess the risks of carcinogenicity and other health effects not documented in the literature.

Although neither the Wei T'o or the Bookkeeper process appear to pose serious safety hazards nor adverse health effects, no formal assessments or literature reviews have been made. Therefore, OTA also lists their impact on health as uncertain in table 16. Fluorocarbons, used in both of these systems, can cause asphyxiation and, if decomposed, can release toxic gases. The amount of Freon 12 in the work environment at the Candanian Wei T'o facility was measured and was well below the Threshold Limit Value (TLV) set for freon. Workplace concentrations averaged from 63 to 125 ppm per volume. The TLV is 1,000 ppm per volume.[5]

Because of the uncertainty regarding future regulations on the use of fluorocarbons, the cost and complexity of both the Wei T'o and the Bookkeeper processes may increase. The fluorocarbons used in these processes can be replaced by other compounds, but both effectiveness and safety may be compromised. Substitutes with similar properties are flammable and more reactive. Ethane emissions from the DEZ process should meet existing hydrocarbon regulations. Ethane's contribution to smog and other air pollution is relatively small and will probably not be affected by any changes in these regulations.

The VPD process is a manual process and poses no safety hazards. Early in its development, however, concerns about the carcinogenicity of cyclamates were extended to cyclohexylamines. These concerns have been relaxed. The use of cyclohexylamines as rust inhibitors is extensive in England.[6] However, as with the Wei T'o and the Bookkeeper processes, no formal assessment of cyclohexylamines or the VPD process has been made. Therefore, its effect on health is also listed as uncertain in table 16.

Other Processes

OTA received limited information on several other deacidification and combined deacidification/strengthening processes. The information provided was either insufficient to analyze to the same degree as the other systems discussed, or the development of the process has not progressed far enough to be considered a viable alternative to the Library's DEZ process.

Deacidification Processes

The French process developed by the Bibliotheque Nationale uses essentially the same chemistry as the Wei T'o system. A pilot-scale plant began operation at the Conservation Center at Chateau de Sable during the fall of 1987 with a capacity of 300 books per 8-hour shift. The system has been described as using more solvents than the Canadian system, which may result in problems with certain inks running.[7] The Bibliotheque Nationale plant is still in its trial period as of this writing, but the developers report analyses show uniform treatment and good alkaline reserve. The developers also plan to conduct their own evaluation during 1988.[8]

The Kathpalia process uses ammonia in a sealed chamber. The process has been used in India by the National Library and National Archives as early as 1955. Current costs are about 30 cents per volume that is 4 inches thick in a chamber that holds 350 volumes.[9] Major criticisms of this system are that it does not provide an alkaline reserve and bad odors are associated with the process. Kathpalia responds to these criticisms by stating that a reserve is not really needed if the books are stored properly and even if they do need to be retreated, the process is so inexpensive it is not a problem. He also responds that odors can be eliminated with adequate ventilation. OTA has not examined this process in detail, but conventional wisdom is skeptical of amine-based processes. Detailed evaluations of the current condition of books that were treated with this process back in the 1950s might be enlightening.

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[5] J.M. Elgie, Dupont of Canada, Ltd., Technical Report Prepared for the National Archives of Canada, Apr. 2, 1980.

[6] Personal communication with a Robertson lab representative.

[7] Jean-Marie Arnault, "Mass Deacidification in France," paper presented at the Preservation of Library Materials Conference sponsored by CDNL, with the cooperation of IFLA and UNESCO, Vienna, April 1986, referenced in G.M. Cunha, Mass Deacidification for Libraries, Library Technology Reports, May-June 1987, p. 383.

[8] Jean-Marie Arnoult, Bibliotheque Nationale, letter to Peter Johnson, Nov. 16, 1987.

[9] Yashpal Kathpalia letter to Peter Johnson, Dec. 12, 1987.

Combined Deacidification/ Strengthening Processes

The Austrian National Library is currently deacidifying and strengthening its newspaper collection. The process it has developed is an adaption of the aqueous deacidification process using calcium hydroxide as the neutralizing and buffering agent. In addition, methyl cellulose is added to the solution. The methyl cellulose precipitates out of solution and acts as a laminate to strengthen the paper. After removing the cover, a block of newspapers is immersed in the solution and then shock frozen at −40° C. The frozen block of paper is then freeze-dried and rebound. The Austrian Library is treating about 50 blocks of newspapers per 5-day week.[10]

The German Library in Leipzig is also developing a process based on the aqueous calcium hydroxide solution deacidification system. The German process adds a carrier to the solution that deposits new cotton cellulose fibers, actually putting a new layer of paper over the old.

The British Library is developing a process that would strengthen paper by grafting a polymer onto the paper's cellulose chains. Papers are exposed to a monomer mixture that impregnates the paper. The paper is then irradiated with low-intensity gamma rays, causing the monomer to attach to the cellulose and to polymerize into chains that link with other cellulose fibers.[11] The process can also be used to deposit an alkaline buffer by choosing an appropriate base monomer as co-monomer. The British process is entering engineering development. Current work is focused on a liquid system. After this has been refined, a large-scale system is planned that could treat 100,000 to 200,000 books per year at a preliminary cost estimate of $5 per book.[12] Recent developments on this process were presented by Dr. Clements in a paper titled "Emerging Technologies in Paper Strengthening: Development and Scale-Up of Graft Co-polymerization Technique," at a Conference in West Berlin in October 1987, organized by Internationale Arbeitsgemeinschaft der Archiv, Bibliotheks-und Graphikrestauratoren.

Just when OTA was completing this report, another U.S. firm from Linden, New Jersey announced a new process they had tested, "the Booksavers MGD process." It is a system based on existing industrial processes for mass sterilization of medical products and food ingredients. Ammonia gas, moisture, and ethylene oxide are introduced into a vacuum chamber to react with paper components to form long-chain amines within the cellulose matrix of the book paper. According to the developers, acids are permanently neutralized, the amines provide an alkaline reserve and crosslinking between the reaction products strengthens the paper.

Based on developer claims, the process would appear to have the potential to deacidify, strengthen, and sterilize books with a gaseous process and overcome the safety issue for DEZ and the preselection issue for the Wei T'o process. Tests performed by the developer show increased fold endurance, uniformity of treatment based on pH measurements, stability of pH change, and an alkaline reserve in treated books ranging from 0.85 to 2.14 percent, depending on the pH of the treated book. The developers have a facility that they claim can be modified to treat 20,000 books each day at a cost of $2 to $3 per book. They also claim that preselection is not required and the books can be treated in sealed cardboard cartons.[13] None of these claims has been subjected to independent analyses and OTA has not been able to evaluate these claims.

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[10] For a more detailed description of this process see Otto Wachter, "Techniques for Preserving Newsprint," in G.M. Cunha, Mass Deacidification for Libraries, Library Technology Reports, May-June 1987, pp. 445-458.

[11] D.W.G. Clements, "Emerging Technologies—Paper Strengthening," *Restaurator*, vol. 8, 1987, pp. 124-128.

[12] D.W.G. Clements letter to Peter Johnson, July 31, 1987. The cost estimate covers direct costs, overhead, and depreciation of capital.

[13] Vladimir Zwass letter to Peter Johnson, Dec. 18, 1987.

ALKALINE PAPER PRODUCTION

One potential long-term solution to the problem of acid deterioration of books is to print books on acid-free, or alkaline, paper.[14] Alkaline paper has a much longer life than acid paper. If all new books were printed on alkaline paper, then it would not be necessary to deacidify them. This section discusses the current status of alkaline paper production and the advantages and disadvantages associated with converting from acid paper production.

Status

Major differences between alkaline and acid paper include the type of sizing that is used to prevent ink from penetrating through it and the type of filler used to make the paper smooth and opaque and to improve printing properties. For alkaline paper, two main types of synthetic sizing materials are used that are active on the alkaline side: alkyl-ketene-dimer (AKD) and alkenyl succinic anhydride (ASA). Calcium carbonate is generally used as the filler and alum is not required as a coreactant. These materials have become popular in Western Europe and have a strong foothold in the U.S. market. But, most paper in the United States is made using rosin/alum sizing and kaolin clay filler, which results in acidic paper.

Calcium carbonate has been used in printing and writing paper production since the 1950s. It was introduced not for its advantages to longevity, but as a way of using byproducts from a pulping process. Calcium carbonate adds brightness and helps promote good print quality through improved ink receptivity. Calcium carbonate is a natural pH buffer to acidic materials. Papers made with it have an alkaline pH, i.e., above 7. Since calcium carbonate will decompose under traditional acidic papermaking conditions, it must be employed in an alkaline papermaking system.

There is general agreeement that the market for acid-free paper is growing, although it remains small relative to total book paper production. Estimates published during the 1980s for the proportion of alkaline paper out of overall book paper range from 15[15] to 25 percent.[16] One source projected a 10-percent increase in the share of alkaline paper through the 1990s.[17]

According to the American Paper Institute, there are no statistics breaking out the volume of alkaline paper produced, or the number of companies producing it. About 30 companies make book publishing paper. Thirteen of these produce 20,000 tons/year or more, including three that produce 100,000 tons/year or more. Two out of the top three companies have alkaline systems. There are about 200 corporations operating a total of about 1,000 pulp and paper mills in the United States today. Therefore, the 30 companies making book paper represent 15 percent of the total number of paper companies.

Alkaline paper is more firmly established in Western Europe (with the exception of Scandinavia) than in the United States. The percentage of acid-free book paper production in Europe is probably about 50 to 65 percent of the total. Among other reasons for the growth of alkaline paper making there, Europe has large easily mined chalk (calcium carbonate) deposits while clay is limited and relatively expensive.

Advantages of Alkaline Paper to Paper Manufacturers

Alkaline paper can provide several cost-saving advantages to paper manufacturers for raw materials, pollution control, maintenance expenses, and production volume. However, these advantages are highly specific to individual plants. Other advantages relate to paper quality and longevity. While most manufacturing costs (e.g., labor) are comparable for acid and alkaline paper of similar quality, some manufacturers find cost advantages in switching to alkaline processes.[18]

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[14] The Council on Library Resources Committee on Production Guidelines in its 1982 report "Book Longevity" has recommended that several categories of books be printed on acid-free paper. These were primary printed sources, important works of fiction and nonfiction, collected editions, bibliographies, guides to collections, yearbooks, gazetteers, scholarly periodicals and monographs, dictionaries, encyclopedias, and other reference books. Categories that need not be on acid paper were also suggested to be textbooks, anthologies, vanity publications, athletic and political hagiography, popularizations in all fields, novelizations of films, formula novels, and most paperbacks.

[15] Chandru J. Shahani and W.K. Wilson, "Preservation of Libraries and Archives," *American Scientist*, vol.75, May-June 1987, pp. 240-251.

[16] Library of Congress, "Paper Durability for Book Longevity," Technical Note 116, Herald of Library Science, vol. 22, July-October 1983; and Committee on Production Guidelines for Book Longevity, Council on Library Resources, Inc., "Book Longevity," 1982.

[17] Conversation with Tom Lord, James River Corp., July 31, 1987.

Cellulose fiber is the most important raw material in paper. For mills that have to buy fiber on the open market in particular, the price of fiber is an important cost in paper manufacturing. Because of the chemically reactive synthetic sizing, alkaline paper is stronger than acid paper. Thus, manufacturers can lower the fiber content of paper while increasing filler and ash content, and get equivalent strength for less cost.[19] Estimates of savings range from $25 to $45 per ton for some grades. While not all types of paper can use increased amounts of filler, more than half the market could benefit. The incentive to lower fiber content is increasing, as the price of fiber is rising.[20]

This potential cost advantage of the alkaline process is probably the most important factor in increasing the market share of alkaline paper. However, its impact may be limited. Large paper manufactureres usually own their own pulp mills, often located close to the paper mill. The cost of fiber for these manufacturers is low. Therefore, the economic advantage for conversion would be less than for many smaller firms. In some cases reduced fiber content may be a disadvantage to manufacturers, as discussed later.

Another cost savings for raw materials applies to some specialty papers. Calcium carbonate can substitute for titanium dioxide, which is more expensive and more difficult to obtain.

Pollution control costs may be lower for alkaline production. Effluent from acid paper making has to be adjusted by adding alkaline materials. No adjustment is needed for effluent from alkaline processes, which comes out with pH near neutral. Also, alkaline effluent has less biochemical oxygen demand (BOD), reducing the BOD load at waste treatment plants.[21] Another environmental advantage for alkaline paper making is the reduction of specific pollutants of concern generated in acid paper making, such as aluminum.[22]

The importance of these benefits varies. Pollution abatement advantages are usually substantial for the large plants that produce the bulk of U.S. paper. Most large U.S. paper plants have pulp mills and wastewater treatment facilities co-located onsite. Pulp mills produce far more effluent than paper manufacture, and if a company can treat pulp mill effluent, it has little problem treating paper plant effluent.

Some maintenance costs may be lower for alkaline production. To reduce water consumption, most paper making companies recycle the water used in manufacturing. When water from acid processes is recycled, alum buildup is experienced, and the system needs to be purged periodically. Compared witht he alum/rosin process, less alkaline filler is lost during paper making.

Whether switching to alkaline processes brings cost advantages depends on the specific circumstances of the manufacturer. One manufacturer reported that while the problems encountered are different, there were no major advantages to alkaline in terms of their cleaning needs. Some firms would need to modify their bacteriological control systems if they were to convert to alkaline paper production.

Decreased water consumption is another possible benefit, to the extent that alkaline processes enable increased recycling.

Alkaline paper processes are less corrosive than acid processes to paper-making machinery. For some manufacturers the advantages of this apply mainly to older non-stainless steel equipment. However, the corrosion advantages of alkaline processes are tangible even for stainless steel.

Some mills can produce greater volumes of alkaline paper than acid paper per unit of time because of differences in water retention. For example, if a mill is drier limited, it can make it go faster and boost production.

Other potential advantages of alkaline production relate to paper quality and longevity. Alkaline paper has greater strength than acid paper. The alkaline process also produces advantages in other areas of quality: alkaline paper is brighter, more opaque, and smoother, which improves print quality and color reproduction. It also reduces mottling. These potential benefits depend on paper grade, the quantity of filler used, the specific type and quality of the calcium carbonate pigment used, and other material and equipment changes.

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[18] Jay W. Brown, "The Once and Future Book: The Preservation Crisis," Wilson Library Bulletin, May 1985, pp. 591-596.

[19] Conversation with Terry Norris, July 7, 1987, Jan. 11, 1988.

[20] Conversation with Robert Olsen, P.H. Glatfelter, July 9, 1987.

[21] Conversation with Robert Olsen, P.H. Glatfelter, July 9, 1987.

[22] Conversation with Tom Commeau, Champion International, July 15, 1987.

Although the market for alkaline paper is not particularly strong at present, some in the paper industry believe the advantages of alkaline paper in longevity will become increasingly important to publishers and their clients.

Disadvantages of Alkaline Paper to Paper Manufacturers

Despite the advantages listed above, there are important obstacles to increasing the role of alkaline paper in paper manufacturing including low demand and the costs of conversion. Growth in the share of alkaline production will be slow until these obstacles are lessened.

The market for alkaline paper, while growing, is not strong enough to motivate major increases in production by paper manufacturers. In general, most U.S. publishers and their customers do not see sufficient advantages to alkaline paper to cause them to select it over comparably priced acid paper.

Publishers are constrained by lack of demand from commercial booksellers. Whether or not a book is printed on alkaline paper is not an important consideration for most buyers at the retail level.[23] The main demand for acid-free books comes from libraries, which account for about 10 to 15 percent of total publishers' sales.[24]

The effects of low levels of demand are compounded by the size of the book paper market. Book paper is a small part of total writing/printing paper production, and an even smaller part of total paper production. In 1986, about 78 million tons of paper and paperboard were produced, out of which 20.5 million tons were printing/writing paper. Book paper accounted for 950,000 tons, less than 5 percent of printing/writing paper and less than 2 percent of total paper production.[25]

Most of the paper used in U.S. books comes from companies whose main products are not book paper. Perhaps one-quarter of book paper comes from companies whose main product is such paper, and who might be expected to be more sensitive to whatever demand exists for paper longevity. The remainder is manufactured by companies with diversified product lines. In many cases, book paper accounts for only a small fraction of the total sales of paper makers. It appears that there is little incentive on the production side to change manufacturing processes at this time.

Switching to alkaline production can be costly for manufacturers, and switching to alkaline paper brings costs to users. Many producers and customers do not want to take the time and effort to adapt their processes to something new. Since a top management commitment to invest in the "learning curve" of a new process would be needed, paper manufacturers would require a similar commitment from their customers.

For manufacturers, switching to alkaline paper may involve substantial retrofitting costs. Depending on the mill, new chemical preparation systems will be required, incorporating different internal sizing, mixing, and storage equipment. The cost may be over $1 million for even a medium tonnage paper mill.[26]

Another factor affecting cost is how calcium carbonate is obtained. Some manufacturers have chosen to build a plant onsite to make calcium carbonate precipitate, thereby gaining good quality control—important in assuring that calcium carbonate particles will be uniform in size. However, such plants are expensive, about $10 million. The other route is to buy fine ground calcium carbonate direct from quarries, with some sacrifice in quality. Depending on transportation costs, buying from quarries can be cheaper than building a plant.

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[23] Jay W. Brown, "The Once and Future Book: The Preservation Crisis," Wilson Library Bulletin, May 1985, pp. 591-596.

[24] Lauren Jackson-Beck, "The Problems of Preservation: Can Librarians and Publishers Solve Them?" *Collection Building*, summer 1985, pp. 21-25.

[25] Conversation with James Hutchison, American Paper Institute, July 14 and 23, 1987.

[26] Conversation with Tom Commeau, Champion International, July 15, 1987.

Alkaline sizing materials are also $1.00 to $1.50 per dry pound more expensive than acid sizing and it is therefore slightly more expensive ($0.50 to $1/ton) to make alkaline paper water resistant.[27] Although to some the increased expense of water resistance could be an important impediment, for most these costs are not significant obstacles to the spread of alkaline paper-making.

Probably the most important disincentives to the spread of alkaline paper-making are the general problems of changing over to a new system. Mills operate on modest margins and high production rates, and taking the time to learn new methods is costly. Similarly, customers used to acid paper may have to make adjustments in dealing with a new product. For example, some dyes that work with acid paper do not work well with alkaline paper. Also, alkaline paper has different "runnability" characteristics than acid paper—that is, it feeds through machinery differently. Industries making envelopes, tablets, etc. have had to change some of their manufacturing procedures.[28] In particular, operators have had to slow down the machinery that converts paper from rolls to single sheets and other products. It is likely that this problem will be resolved within a few years, this has affected the acceptability of alkaline paper to some important categories of users.

Adjustments in processes (e.g., in altering dyes) are relatively easy. With adjustments, alkaline paper is equal to or better than acid paper for most uses. Still, without a cost differential in favor of alkaline paper, there is little incentive for end users to take the effort and cost of dealing with conversion problems—and little incentive for paper manufacturers to risk sales by introducing alkaline in place of acid paper.

As mentioned above, one of the main selling points of the alkaline process is its potential for saving costs through fiber reduction. This also has a down side. Many customers of paper manufacturers (e.g., makers of envelopes) sell large quantities of waste paper to recyclers, often deriving substantial revenue. Rising pulp prices have made waste paper more attractive as a raw material.[29] There is concern by these customers that decreasing the fiber content of the paper they use will make the waste paper less attractive to recyclers. In turn, paper manufacturers considering alkaline processes are concerned that their clients might prefer acid paper for this reason.

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[27] Conversation with Jay Vreeland, S.D. Warren, July 9, 1987.

[28] R.G. Johnson, "U.S. Alkaline Fine Papermaking To Experience Slow But Steady Growth," *Pulp and Paper*, December 1986, pp. 66-67.

[29] *Paper Chemicals Markets in Europe* (New York, NY: Frost & Sullivan, Inc., 1982), p. 32.

DISCUSSION

No mass deacidification systems are operating or are being built, designed, or planned on the scale envisioned for the Library's DEZ full-scale facility (over 1 million books per year).

One mass deacidification pilot plant using a Wei T'o system is in operation at the National Archives of Canada. This plant has been in operation for 7 years and treats about 40,000 books per year—roughly the capacity of the Library's DEZ pilot plant built for engineering testing in Texas. The "Bookkeeper" process has also been developed and a pilot plant system has been designed. The system has yet to be built but it would have a capacity on the order of the DEZ and Wei T'o pilot plants. Other systems of a much smaller scale are in operation (a Wei T'o spraying system at Princeton and an aqueous deacidification and strengthening system in Austria), the French are testing a small pilot plant based on the Canadian design, and the English have just begun to design a small-scale system that would both strengthen and deacidify books, but this is still at a very early stage of development.

Only two processes, Wei T'o and the Bookkeeper have had sufficient development at the scale required by the Library to merit consideration as options to the DEZ process at this time.

There have been no independent tests or evaluations of the cost and effectiveness of these processes. All data and estimates have been developed by the firm or organization that is promoting the process (including the Library). Without some independent analyses with standard test materials and procedures, a definitive comparison of the processes cannot be made.

In general, all of the processes neutralize the acids present in the paper. Each of the developers present data that indicate their process can extend the life of a book by roughly the same amount (two to five times), based on fold endurance after accelerated aging. Other supporting analyses are limited mainly to pH measurements and alkaline buffer contents, resulting in a limited amount of information on which to assess the processes.

With this in mind, a qualitative evaluation of the advantages and disadvantages of the three principle mass deacidification processes follows.

The DEZ system is capable of treating books with a high degree of uniformity. The zinc oxide buffer can be controlled and leaves the paper relatively neutral regardless of the paper's initial acid content. It is compatible with most other book materials, especially inks and pigments, and requires little or no preselection. It is also capable of treating other formats. Health and environmental impacts of the system are considered to be minimal, but are currently or will soon be investigated in greater detail.

The key technical disadvantage of the DEZ system is that safety is a critical issue in the operation of the plant and requires added costs to manage. There are small but serious risks to plant workers and equipment and to a limited extent, the public (i.e., during the transportation of DEZ to the plant). It is also capital intensive and requires a relatively large initial investment.

The Wei T'o system is based on a chemistry that is accepted in the preservation community. The pilot plant in Canada has been in operation for 7 years. Unfortunately, development of the system has not progressed much during that time, although the operation of the plant is routine. The Wei T'o system is currently moderate in cost and investment. It is relatively safe compared to the DEZ plant. Although the health impacts of the process are not considered to be problem, they have not been formally assessed.

The principal disadvantage of the Wei T'o process is that its solvents are not compatible with a number of common book materials and artifacts (i.e. stamp inks, label adhesives, certain pigments, and certain plastic laminated book covers). The Canadian operation rejects 20 to 25 percent of the books sent for treatment. The amount of alkaline buffer appears to be less than that deposited by the DEZ process and varies with the concentration of the solution and the initial acid content of the papers. There are no data describing the uniformity of the treatment. One book picked at random during an OTA visit showed non-uniform treatment of the pages. The amount of fluorocarbons released during the total process is below current regulations. However, the uncertainty about future regulations makes investment and operating costs more uncertain.

The Bookkeeper process is the simplest of the three. It has the shortest cycle times, requiring no drying as do the other two processes, and capital investment would probably be low. Because of the chemicals it uses, compatibility with inks, colors, etc. is not expected to be much of a problem, although not enough tests have been conducted to determine what, if any, preselection is necessary (e.g., plastic covers may be a problem as with the Wei T'o process). Tests by the developer have shown that treatment can be uniform throughout the book and page. The alkaline buffer does not depend on the moisture or initial acid content of the paper. Health impacts are not considered a problem, although no formal assessment has been made.

The primary disadvantage of the Bookkeeper process is that it relies on its alkaline reserve to neutralize the paper over time. Although fold endurance tests after aging show results similar to those of the DEZ process, the depletion of the alkaline reserve would be expected to be faster. Uncertainty about future regulation of fluorocarbons makes capital and operating costs uncertain. Also, the level of development of the total system is behind that of the DEZ and the Wei T'o systems.

The use of alkaline paper in books is not expected to grow significantly in the near future. The advantages and disadvantages of switching to alkaline paper varies from producer to producer and publisher to publisher. The major factor inhibit-ing a wider conversion is that book paper makes up a small percentage of the paper market, and the library community and those interested in preservation make up an even smaller percentage.

Since there are no reliable data to estimate the trends in the use of alkaline paper, OTA cannot make a quantitative estimate of costs to switch to alkaline paper. It would be desirable, however, to compare alkaline paper production costs to future deacidification costs for some category of books or materials that end up being valuable in library collections. Prior to making such estimates, however, the library community would need to select and agree on those categories. While such an approach would not have any effect on the brittle book problem of today, or even a few years from now, it might result in substantial savings in the long run.

Appendixes

Appendix A

Definition of Terms

Accelerated Aging: exposing paper to high temperatures and varying humidity to simulate natural aging.

Acid Books: books whose pages have a pH of less than 7. The pages are not yet brittle, but because of their acidity they will become brittle in time.

Acid-Free: paper or books made with paper produced by alkaline manufacturing processes. Although the paper may not be totally free of acid, its pH is nearly neutral.

Aqueous Solvent: water or watery substance used to dissolve chemicals.

Autocatalytic: a self-sustaining decomposition of a chemical compound, often accompanied by a very rapid release of energy.

Brine Seal Tanks: seal pots that use brine to neutralize DEZ.

Brittle Books: books whose pages have become so fragile that they cannot be circulated.

Cellulose: primary plant fiber used to make paper.

Compatible: indicates that a chemical or process has no adverse reaction with the various materials or chemicals found in books (e.g., the paper's cellulose, sizing, fillers, pigments, inks, glues, labels, covers, etc.).

Dew Point: temperature at which vapor condenses into liquid.

Distributive Control System (DCS): a computer system that monitors and helps to operate chemical processes.

Fold Endurance: the number of folds a piece of paper (under tension) can withstand before it breaks (see TAPPI standard - T511.50-69).

Hemicellulose: a substance like cellulose, but less complex.

Inert Gas: gas such as nitrogen, having few or no active properties.

kPa: kilopascal, a unit of pressure roughly equal to 1/100 of atmospheric pressure.

Lignin: unstable constituent of wood pulp that leads to rapid deterioration of paper.

Load Cells: devices used to measure weight.

Loss Time Accidents: industrial mishaps that result in worker(s) not being able to return immediately to work.

Mass Deacidification Process: chemical treatment to neutralize acids in paper and provide an alkaline buffer that can handle several closed books at one time.

Metal Alkyls: a chemical compound linking a metal atom or atoms with a hydrocarbon radical of the form C_uH_{2n+1}; very reactive.

Nonaqueous Solvent: chemicals (other than water) used to dissolve other chemicals. Nonaqueous solvents used in deacidification techniques include methanol.

Paper Brightness: ability of a paper to reflect light.

Paper Durability: relates to the physical and mechanical properties of paper

and its ability to resist wear and tear.

Permanent Paper: paper that is usually acid-free and is made to resist the effects of aging to a greater degree than ordinary paper.

TAPPI Standards:
Type I - Maximum Permanence
pH = 7.5 - 9.5 + 2 percent $MgCO_3$ or $CaCO_3$
Type II - High Permanence
pH = 6.5 - 8.5
Type III - Medium Permanence
pH greater than 5.5

Paper Permanence: ability of paper to maintain any or all of its properties over time.

Permissives: a specified set of process parameters (including interlocks) that must be met before starting the next process step.

pH: a measure of acidity (or alkalinity). On a log-scale from 0 to 14, a pH of 7 is neutral. A pH less than 7 indicates the presence of acids, a pH greater than 7 indicates the presence of alkaline materials.

Plant Commissioning: starting up and checking out, both individually and as a system, the various pieces of equipment to be used in a processing plant.

Polymerization: the process of joining two or more like molecules into a more complex molecule whose molecular weight is a multiple of the original and whose physical properties are different.

Preselection: screening to determine which books can be safely treated.

PSIG: pounds per square inch gauge; pressure measured relative to atmospheric pressure which equals 14.7 pounds per square inch.

Pyrophoric: chemical that spontaneously ignites when exposed to air.

Safety Interlocks: a specified set of positions for various pieces of equipment (e.g., on/off or open/closed) that must be met before another operation can occur.

Seal Pot: tank containing agents that can neutralize DEZ; used to remove DEZ vapors from effluent vapors before releasing them to the atmosphere.

Sizing Agent: material added to paper during manufacture to reduce penetration of liquids and prevent inks from blotting.

Specific Heat: the heat required to raise the temperature of one gram of a substance one degree Centigrade.

Strengthening techniques: methods for restoring brittle papers so that they can be handled.

Surfactant: a chemical used in a liquid dispersion to keep other particles equally dispersed within the liquid.

TAPPI: Technical Association of the Pulp and Paper Industry.

Thermochemical Properties: characteristics dealing with the interrelation of heat with chemical reaction or physical change of state.

Thermodynamic Properties: characteristics dealing with mechanical action or heat.

Threshold Limit Value (TLV): a maximum level of exposure set by the American Conference of Governmental Industrial Hygienists (ACGIH) for various industrial substances.

Titration: chemistry method for determining the strength or concentration of a solution.

Torr: a unit of pressure equal to 1/760 of atmospheric pressure.

Appendix B

Library of Congress' Operating Cost Estimates for Full-Scale Mass Deacidification Facility

November 1987

This appendix contains the estimates of operating costs for a full-scale mass deacidification facility prepared by the Library of Congress and submitted to OTA as of November 1987. All estimates are preliminary and subject to refinement based on results of tests at the Texas Alkyls pilot plant. The appendix consists of three parts:

1. The basis for costs describing assumptions used to develop operating cost estimates.
2. Cost tables and discussion showing operating cost estimates at different production rates in terms of total treatment costs, per-book costs, and detailed costs for a facility treating 1 million books per year. These detailed costs are further explained in a series of notes.
3. Standard operating costs that are not applicable to the proposed facility.

Basis for Costs

Preliminary annual operating costs for the Ft. Detrick Book Deacidification Facility are based on two to four T/V Chambers operating on a 72-hour treatment cycle or less for 24 hours per day, 7 days per week, and 350 days per year.

A checklist to aid in determining the Annual Operating Costs was prepared by modifying a similar table in *Perry's Chemical Engineers' Handbook* (Perry, Chilton, Kirkpatrick, 4th ed., McGraw-Hill, 1963). This checklist was prepared in two parts: Part 2 - table B-1 includes all those items assumed applicable to a government-owned installation at Ft. Detrick, and Part 3 lists those items not applicable.

Part 2 - tables B-2 and B-3 show for the Ft. Detrick Facility a summary of the annual operation costs in dollars per year and in dollars per book, respectively, for four annual production rates.

The cost of book handling at the Library and book transportation to and from the plant are not included as part of plant operating costs because these tasks would have to take place independent of the process used. Previous estimates placed this figure at approximately $0.70 per book.

Contractor supervision and operation of facility is assumed.

Operating data, soon to be obtained from the Texas Alkyls Small Scale Test Deacidification Facility in Deer Park, Texas, will be used to refine the cycle times and the number and the capacity of T/V Chambers. With these data and from the design of the Ft. Detrick Facility the costs estimated in table B-1 will be updated.

Cost Tables and Discussion

Table B-2 shows the major annual operating costs for four production rates.

Table B-3 converts the dollar costs in table B-2 to dollars per book treated.

Table B-1 is for an annual capacity of 1 million books, and shows a breakdown of costs for each group of costs shown in table B-3.

Items Not Applicable to the Ft. Detrick Facility

1. Plant Costs
   - Company contribution of profit sharing or thrift plan
2. Plant Overhead
   - Purchasing
   - Personnel and industrial relations
   - Automotive and rail switching
   - Plant hospital and dispensary
   - Cafeteria and club rooms
   - Taxes on properties and operating licenses
   - Insurance - property
   - Depreciation
3. Distribution Costs
   - Containers and packages
   - Freight
   - Operation of terminals and warehouses
   - Wages and salaries plus fringe benefits
   - Operating materials and utilities
   - Rental or depreciation

Table B-1.—Breakdown of Annual Operating Costs at 1 Million Books per Year

Product	Deacidified Books
Producer	Contractor to the Library of Congress
Location	Ft. Detrick, MD
Byproducts	Ethane and water extracted from books
Process	Under vacuum: books dehydrated, diethylzinc reacted with remaining water and acid and rehydrated
Operation	Batch cycles
Annual capacity	500,000 to 2,000,000 books per year
Fixed investment	See Appendix C: Capital Cost Estimate
Stream days	350 24-hour days

Cost Component	Dollar cost per year
1. *Plant Costs*	
1.1 Raw Materials	
—Standard Test Books	$ 13,000
1.2 Processing Chemicals	
Diethylzinc	800,000
—Treated Water	3,000
—Nitrogen	30,000
1.3 Operating Supplies	
—Dowtherm J	500
—Lubricating oil	2,000
—Kerosene	500
—Refrigerant	1,000
—Supplies/Sundries	3,000
1.4 Utilities	
—Electricity	70,000
—Cooling Water	10,000
—Instrument Air	1,000
—Steam	3,000
1.5 Maintenance Materials*	60,000
Subtotal: Plant Costs	$997,000
2. *Operating Labor*	
2.1 Plant manager	$ 65,000
2.2 Operation engineer	45,000
2.3 Chemical/computer technician	40,000
2.4 Eight operations/technicians/book handlers @ $32,000	256,000
2.5 Day shift maintenance person	35,000
2.6 Outside maintenance support on demand	20,000
2.7 Total direct labor	$461,000
2.8 Payroll burden (fringe benefits) for Federal OASI, Workman's Compensation Insurance, contributions to pension, life insurance, thrift plan, vacations, holidays, sick leave, overtime premium	152,000
Subtotal: Operating Labor	$613,000
3. *Plant Overhead*	
3.1 Administration (by plant manager)	see 2.1
3.2 Indirect labor	
—Laboratory technician	$ 28,000
—Secretary/receptionist	22,000
—Technical service & engineering	Note 14
—Shops and repair facilities	Note 15
—Shipping and receiving department	Note 16
—Payroll burden of 3.2 Indirect Labor	17,000
3.3 Inspection, safety and fire protection	Note 17
3.4 Accounting, clerical and stenographic	Note 18
3.5 Communications: telephone, mail, teletype, modem	3,000
3.6 Plant custodial	10,000
3.7 Plant protection	Note 17
3.8 Waste disposal	10,000
3.9 Insurance, third party liability	20,000
Subtotal: Plant Overhead	$110,000
4. *Administrative Expense*	
Contractor's fee taken as 15 percent of 2.0 Operating Labor subtotal, $613,000, plus $67,000 of 3.2 Indirect Labor	$102,000
Total Annual Operating Cost for 1 Million BPY at Ft. Detrick	$1,822,000

*Replacement parts, repair of equipment, etc.

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1. 1.1 Raw Materials - The books to be treated are not considered a cost item but Standard Books for quality control are.
2. 1.2 Processing Chemicals: DEZ usage, the major chemical cost, is based on an average 1½ percent DEZ being laid down in an average 1.86 pound book which is equivalent to 72 cents per book for $17.00 per pound DEZ. Until better operating data is obtained 8 cents was added for small losses and wastage, e.g., equipment and line cleaning, to develop the 80 cents.
3. Other Chemicals: How much 1.2 Nitrogen (considered a processing chemical for purging, particularly, the T/V Chambers) to be used, is now a guess taken as 250 tons * $120/ton @ $30,000.
4. 1.3 Operating Supplies: Dowtherm J, used as the heat transfer oil, may be needed for periodic replacement. The replacement cost is estimated at about $500 per year. Lubricating oil for the pumps will probably require changes costing an estimated $2,000 per year. Kerosene, the sealant for the two Seal Pots, and for clean out of equipment is a minor cost. Supplies/sundries: other lubricating oils, greases, about $3,000 per year for refrigerant, chemicals for the laboratory and gasket replacement, all usually a minor cost item, will be better known toward the beginning of spring 1988.
5. 1.4 Utilities: The amount of electricity, the major utility cost item for power, lighting, refrigeration and air conditioning, will be better known in the spring of 1988 after a few small scale tests and the redesign of the Ft. Detrick deacidification facility. It is estimated now as 1,400,000 kWh @ 5 cents/kWh = $70,000. Cooling water, instrument air, and steam (for heating comfort) are minor utility cost items.
6. 1.5 Maintenance Materials - Taken as a percentage of the chemical processing part of the Ft. Detrick Facility.
7. 2. Operating Labor - There will be better data from the Small Scale Plant Operations but the labor for Ft. Detrick remains a good but tight estimate until Ft. Detrick is in operation. There will be more clarification for job assignment and responsibilities details. It is assumed that one of the two shift operators will assist in DEZ cart movement and assist in the Quality Assurance Laboratory.
8. 2.1. A Plant Manager or similarly titled person is needed to be in charge and to interface with Ft. Detrick and Library management. The same person, after the start-up period, should have ample time to manage other operating sites. Thus, a smaller cost than the $65,000 salary plus benefits could be required.
9. 2.4. Eight operations/technicians/book handlers are determined as two people per shift for 168 hours per week @ 40 hours per person = 8.4 people. Assume some of the eight will work overtime to cover for 0.4 person, sick leave, vacation, holidays, jury duty, military service, etc. The two operators per shift was chosen based on the emphasis on safety even though there may not be sufficient activities to occupy two people after start-up and the plant is run routinely.
10. All book movements at the facility are planned to be done by the operators.
11. 2.5. Direct Maintenance Labor - These costs will be better defined after the redesign of the Ft. Detrick facility and the operation of the pilot plant.
12. 2.8. Payroll Burden on all Labor Charges - this major cost item, lumped as one percentage of labor for all benefits as defined in Reference.
13. 3.1 Administration - This is assumed under 2.1 Plant Manager.
14. Technical service and engineering will be by contractor and covered under administrative expense.
15. Shops and repair facilities are included under maintenance labor.
16. Shipping and receiving department to be handled by shift operators.
17. Inspection, safety and fire protection and plant protection provided by Ft. Detrick.
18. 3.4. Accounting provided by contractor and secretary/receptionist does clerical and stenographic.
19. 3.8. Waste Disposal of 10,000 gallons at $1.00/gallon = $10,000.
20. 4. Administrative Expense: Contact was made with contracting companies in a somewhat similar position to establish the rate of 15 percent and its basis. Also see Notes 14 and 15 preceding.

4. Marketing Costs
5. Administrative Costs
    - General account, clerical auditing
    - Central engineering and technical
    - Legal and patent
    - Within and outside the facility
    - Payment and collection of royalties
    - Contributions and dues to associations
    - Financial
    - Debt management
    - Maintenance of working capital
    - Credit functions
    - Communications and traffic management
    - Central purchasing activities
    - Taxes

Table B-2.—Annual Operation Costs in Dollars per Year

	Capacity in millions of books per year (dollars per year)			
Cost components	0.5	1	1.5	2
Plant costs	$ 551,000	$ 997,000	$1,450,000	$1,897,000
Operating labor	611,000	611,000	611,000	611,000
Plant overhead	110,000	110,000	110,000	110,000
Administrative expense	102,000	102,000	102,000	102,000
Total unit treatment cost at Ft. Detrick	$1,374,000	$1,822,000	$2,273,000	$2,720,000

Table B-3.—Annual Operation Costs in Dollars per Book

	Capacity in millions of books per year (dollars per book)			
Cost components	0.5	1	1.5	2
Plant costs	1.10	1.00	0.96	0.95
Operating labor	1.22	0.61	0.41	0.31
Plant overhead	0.22	0.11	0.07	0.05
Administrative expense	0.20	0.10	0.07	0.05
Total unit treatment cost at Ft. Detrick	2.74	1.82	1.51	1.36

Appendix C

Library of Congress' Capital Cost Estimates for Full-Scale Mass Deacidification Facility November 1987

This appendix includes the estimates of capital costs for a full scale mass deacidification facility prepared by the Library of Congress and its contractors in November 1987. This facility would be composed of two structures, a warehouse support building and a chemical treatment building. The appendix consists of four parts:

1. The cover memorandum provides some of the major assumptions used to come up with the estimates.
2. Table C-1 lists the construction costs for the chemical treatment facility.
3. Table C-2 lists the space requirements for the different components of the warehouse support facility and the estimate of costs to construct such space.
4. Table C-3 lists the changes in equipment that will probably be required to scale-up the Texas Alkyls pilot plant into a full-scale facility that can treat 1 million books per year.

Table C-1.—Capital Cost Estimate for a One-Million-Book-Per-Year Deacidification Chemical Process Facility

Item	Cost estimate
Concrete	$ 40,000
Steel	40,000
Equipment	875,000
Spare Parts (Inventory)	50,000
Pipe	250,000
Electrical	275,000
Instruments	450,000
Building (Shell)	[a]
Insulation	50,000
Coatings	20,000
Fire Protection	50,000
Field Indirects	300,000
Engineering and Home Office	190,000
Fee	200,000
Total	$2,750,000

[a] Included in total space and capital estimate for warehouse/processing facility.

Table C-2.—Capital Cost Estimates for a Deacidification Plant Office/Warehouse Support Facility

		Square feet
1.0	Administration	
1.1	Vestibule	75
1.2	Reception and Waiting	190
1.3	Plant Manager	120
1.4	Operations Engineer	100
1.5	Chemical/Computer Technician	100
1.6	Office	100
1.7	Office	100
1.8	Copy	80
1.9	Storage	80
1.10	Toilets (2 @ 80 SF)	160
1.11	Janitor Closet	35
1.12	First Aid	165
1.13	Lunch Room	250
1.14	Conference Room w/Screen	300
	Subtotal	1,855
2.0	Warehouse/Processing	
2.1	Pallet Storage	8,000
2.2	Chemical Process Area	8,000
2.3	Quality Assurance Laboratory	750
2.4	Maintenance	1,100
2.5	Men's and Women's Lockers	400
2.6	Loading/Unloading	1,050
2.7	Spare Parts Storage	1,000
2.8	Service Dock	300
	Subtotal	20,600
3.0	Building Support	
3.1	Mechanical Room	1,500
3.2	Electrical Room	1,000
3.3	Telephone Equipment Room	120
3.4	Building Maintenance Room	120
	Subtotal	2,740
	Support Building Area:	8,178
	Support Building Gross:	2,818
	Support Building and Chemical Process Totals (square feet):	30,996

		Gross SF	Cost/SF	Amount
4.0	Building Cost Estimate			
4.1	Administration	2,504	$72.00	$ 180,288
4.2	Warehouse/Processing	22,660	55.00	1,246,300
4.3	Building Support	3,014	55.00	165,770
4.4	Building Walls	3,818	55.00	209,990
	Total Building Cost	31,996		$1,802,348
5.0	Project Cost Estimate			
5.1	Building Cost			$1,802,348
5.2	Site Work			328,000
	Total Project Cost (w/o Process Equipment)			$2,130,348

LIBRARY OF CONGRESS

TO: Mr. Peter Johnson
Office of Technology Assessment

DATE: November 23, 1987

FROM: Peter G. Sparks
Director, Mass Deacidification Program

SUBJECT: Capital Cost Estimates for Main Deacidification Facility

As requested the Library has taken steps to come up with capital cost estimates for the Ft. Detrick facility. These costs were based on our current thinking that the facility would consist of two separate structures--a support facility and a chemical treatment facility. It is unclear at the moment how these structures would be connected but we see this as a minor cost. We worked with the architect that had previously been for the project Shertz, Franklin, Crawford and Shaffner in Roanoke, Virginia and with S&B Engineering in Houston, Texas to get estimates. Both estimates were done in consultation with our engineer who reviewed the chemical plant costs in detail.

The estimates for the warehouse support facility are fairly self-explanatory showing the various functions that will be in the building with gross square footage allocated to each and the construction cost estimate at the end. These data are shown in table C-2.

The estimates for the chemical treatment plant are based on a hypothetical chamber size and configuration since there is no firm design in place for this part of the facility. The chemical part of the facility and the control room flow from the design of the pilot facility. The chemical facility estimates are based on a number of assumptions which are listed below:

1. The four chamber design has been chosen to stay within the capacity of commercially available vacuum pumps.
2. The unit can be installed in a building approximately 100 feet by 80 feet.
3. Utilities such as electricity, instrument air, fire water, and potable water are available at battery limits.
4. No site development work is included.
5. No emergency power generator is provided.
6. Estimate is based on Houston area open shop labor rates.
7. No contingency is added to the estimate.

An analysis of the large scale facility requirements and equipment changes are shown in table C-3. Construction cost estimates for a one million book per year treatment facility are given in table C-1.

Attachments

Table C-3.—Equipment Changes for Scale-UP

1. Design items	Pilot unit as designed	1mm book/year facility
No. of Chambers	1	4
No. Carts in Chamber (27" W x 48" H x 41" L)	—	5
Average No. of Books per Cart	—	224
No. Books/Chamber—Maximum	360	1,120
Design Cycle Length[1]	30.5	36
Cycles/Year/Chamber	—	223
Chamber, Hrs. in Operation	—	8,028
Hrs. Down	—	732
Overall Service Factor	—	91.6
Per Chamber per Cycle, lbs.		
DEZ Consumed	23.31	72.52
C_2H_6 Released	11.35	35.52
Annual Rates, lbs/yr.		
DEZ Consumed	—	64,687
C_2H_6 Released	—	31,505
Chamber, Diameter	6'0"	6'0"
Length	5'6 T-F	10'0" T-F
DEZ Circulation Rate, lbs/hr.	573.8	773.4
N2DD Circulation Rate, lbs/hr.	1,600	4,300

[1] Does not include time to load or unload chamber.

2. Equipment	Pilot unit as designed	1mm book/year facility
DEZ Vaporizer Duty, BTU/hr.	105,000	141,000
DEZ 1st Stg. Condenser Duty, BTU/hr.	120,000	152,500
DEZ 2nd Stg. Condenser Duty, BTU/hr.	17,000	23,000
N_2 Heater/Cooler		
Duty, Heating BTU/hr.	17,500	50,000
Cooling BTU/hr.	20,000	54,000
Rehydration Water Heater		
Duty, BTU/hr.	92,670	288,178
Kw	30	100
Watlow Model	FPN 720 G5	FRN 744 E5
Hot Oil Heater		
Duty, BTU/hr.	130,000	151,000
Kw	40	50
Watlow Model	CFRS 743 E5	CFRS 751 E5
Refrigeration Unit Duty, Tons	11	15
DEZ Receiver		
Diameter	12.09"	17.25"
Height	30" T-T	36" S/S
Rehydration Tank		
Diameter	24" OD	24" OD
Length	18"	50"
Hot Oil Surge Tank		
Diameter	23.25"	35.25"
Height	4'0" T-T	4'6" T-T
Chilled Oil Surge Tank		
Diameter	29.25"	35.25" ID
Height	4'0" T-T	5'0" T-T

Table C-3.—Equipment Changes for Scale-UP—(Continued)

2. Equipment	Pilot unit as designed	1mm book/year facility
Seal Pot		
Number	2	2
Diameter	12.75′ OD	18″ OD
Height	18″ T-T	18″ T-T
Exhaust Blower	(Balzers)	(Balzers)
Suction Pressure	40 Torr	140 Torr
Discharge Pressure	800 Torr	800 Torr
ACFM Suction	128	110
Balzers - Model	DUO 250 A (Two Stg. Rotary Vane)	2 C DUO 250 A
DEZ Recycle Blower	(Balzers)	(Balzers)
Suction Pressure	18 Torr	18 Torr
Discharge Pressure	50 Torr	150 Torr
ACFM Suction	1,505	2,610
Balzers Model	WKP 4000	2 @ WKP 4000
Nitrogen Recycle Blower	(Not Provided)	
Suction Pressure	0 Psig	0 Psig
Discharge Pressure	10 Psig	15 Psig
ACFM Suction	364	1,050
Chamber Vacuum Pump		
Suction Pressure	Oil to 760 Torr	Oil to 760 Torr
Discharge Pressure	800 Torr	800 Torr
ACFM Suction	85	170
Kinney Model	KTC - 112	3 @ KTC - 225
Hot Oil Circulation Pump		
GPM, Rated	67.0	200
TDH, Rated	89.5′	100′
H.H.P.	1.25	4.17
Chilled Oil Circulation Pump		
GPM, Rated	112.5	270
TDH, Rated	88.9′	100′
H.H.P.	2.23	6.12

Appendix D

Suggestion for Standard Paper Testing for Deacidification Quality Control by National Bureau of Standards

This appendix lists procedures recommended for assessing the stability of book papers before and after treatment with diethylzinc. The procedures were recommended by Edwin Parks of the National Bureau of Standards Ceramics Chemistry and Bioprocesses Group. The appendix consists of two parts:

1. List A consists of routine tests suitable for quality control during the engineering program. With the exception of fiber strength analysis by zero span tensile testing, most of the tests have been used by the Library of Congress in their development of the diethylzinc process. One modification of an aging technique is recommended, that is, humid aging at 75° C and 50 percent relative humidity.
2. List B consists of more time-consuming research tools that may not be practical in the context of a large-volume testing program.

Technology for Assessing the Effectiveness of Paper Preservation by Treatment With Diethylzinc (DEZ)

Recommended Procedures

1. Accelerated aging techniques (to be performed before and after DEZ treatments)
    a. *Dry air*
    "Standard test method for relative stability of paper (effect on folding endurance)." ASTM Designation D-776-65
    b. *Humid air*
    (1) 75° C, 50 percent relative humidity
    (2) 90° C, 50 percent relative humidity
    Commercial ovens may be employed, combining wet bulb temperatures of 59.5 and 73° C and dry bulb temperatures of 75° C and 90° C, respectively. Aging periods and sampling intervals to achieve significant decreases in strength will vary with types of paper. Twelve days is likely to be more than sufficient.
2. Testing procedures (to be performed before and after accelerated aging)
    a. *Folding endurance*
    "Standard test method for folding endurance of paper by the MIT tester." ASTM Designation: D-2176-69. Method allows for pressures of 0.5 to 1.5 kg, but even the lowest pressure may be too severe for deteriorated book papers.
    b. *Fiber strength (zero-span tensile strength)*
    Not a standard procedure. Zero-span tensile tests can be performed with an IPC (Institute of Paper Chemistry) zero- span clamp attached to the jaws of a conventional load-elongation machine. However, we recommend a machine dedicated to zero span tensile determinations.
    This is a quick, simple physical test that may be applicable to degraded book papers which would not survive even a single fold, but might still have useful life if the DEZ method prevents further degradation.
    c. *Hot water extractable acidity or alkalinity of paper.* TAPPI method T-428 pm-77. Modifications of the standard method, as proposed by the Library of Congress, should be equally suitable for the extensive routine testing program envisaged.
    d. *Brightness of pulp paper, and paperboard (directional reflectance at 457 mm).* TAPPI standard Method T-452 om-83.

Supplemental Procedures

1. *Standard test method for copper number of paper and paperboard.* ASTM Designation: D-919-74.
    A suggested research technique only, not for routine qualitative assurance testing. This is thought to be a measure of carbonyl group concentration and may be correlated with carbonyl absorbance peak intensities in FTIR spectra. The prospect might then exist to use FTIR as a quick, non-destructive routine test.
2. *Wet tensile breaking strength of paper and paperboard.* TAPPI method T-456 om-822. For research and exploratory purposes only.
3. *Alpha cellulose in paper. TAPPI method I-429 os-78.* Alpha cellulose is a stable polymeric component of paper. This procedure uses strong alkali to extract components of less stability and lower molecular weight; hence, it is potentially useful for following the course of deploymerization during aging processes. A time-consuming and hazardous procedure to be used for specific research objectives, not as a routine test; not useful for papers containing lignin.

Appendix E

List of Papers and Presentations on the DEZ Process by the Staff of the Library of Congress From 1974-86

George B. Kelly	
1974	
"Research on Mass Treatment in Conservation"	Published: *Bulletin of the American Institute for Conservation*, vol. 14, No. 2
1978	
"Mass Deacidification With Diethylzinc, Large-Scale Trials"	Published: *Preprints* - AIC 6th Annual Meeting
"Inhibition of Light Sensitivity of Papers Treated With Diethylzinc"	*ACS Advances in Chemistry Series 193, Preservation of Paper & Textiles of Historic and Artistic Value #2*
1979	
"Non-Aqueous Deacidification: Treatment en masse and for the Small Workshop"	Rutgers University
1980	
"Non-Aqueous Deacidification: Treatment en masse and for the Small Workshop	International Conference on the Conservation of Library and Archive Materials and the Graphic Arts
"Mass Deacidification With Diethylzinc"	Published: *The Library Scene*
Donald K. Sebera	
1980	
"Current Problems in the Convervation of Cellulosic Materials"	Gordon Research Conference, Wolfboro, NH
1983	
"Recent Developments in the Library of Congress' DEZ Mass Deacidification Process"	American Institute for the Conservation of Historic and Artistic Works of Art on Paper, Baltimore, MD
1984	
"Reactions of Diethylzinc With Paper Constituents"	Third Symposium on the Preservation of Paper and Textiles of Historic Value, American Chemical Society, Philadelphia, PA
1986	
"The DEZ Mass Deacidification Process at the Library of Congress"	10th Annual Conference of Institute of Paper Conservation, Oxford, England
"The DEZ Mass Deacidification Process at the Libary of Congress"	Paper submitted for publication in *Studies in Conservation*
"The Library of Congress Mass Deacidification Process"	Paper prepared in response to George Cunha's questionnaire

Peter G. Sparks

1982

Library of Congress' Mass Deacidification/Optical	Library Directors Meeting - May 6
Library of Congress' Mass Deacidification/Optical	Library of Congress Technology Meeting - June 17
Library of Congress' Mass Deacidification Program	NASA/Press Briefing - October 15
Library of Congress' Mass Deacidification Program	Fifth Brazilian Conference on Deacidification Program

1983

Library of Congress' Mass Deacidification Program	IFLA Conference - August 26

1984

Library of Congress' Mass Deacidification/Optical	ALISE - January 7
Library of Congress' Mass Deacidification Program	COSLA - April 11
Library of Congress' Mass Deacidification Program	Senate Committee Hearing - April 11
Library of Congress' Mass Deacidification Program	Simmons College - April 18
Library of Congress' Mass Deacidification Program	Society of American Archivists - August 31

1985

Library of Congress' Mass Deacidification Program	Book Publishers - September
Library of Congress' Mass Deacidification Program	NASA/Goddard Space Flight Center
Library of Congress' Mass Deacidification Program	Federal Interagency Field Program Workshop - November 29

1986

Library of Congress' Mass Deacidification Program	University of Puerto Rico - February 5
Library of Congress' Mass Deacidification Program	National Conference on Museum Security - February 18
Library of Congress' Mass Deacidification Program	IFLA - Vienna Conference on Preservation of Library Materials - April
Library of Congress' Mass Deacidification Program	LITA Institute on Technology - May 6
Library of Congress' Mass Deacidification Program	Special Library Association Military Division - May 8
Library of Congress' Mass Deacidification Program	Frederick City Council Meeting - May 8
Library of Congress' Mass Deacidification Program	ALA Law Librarians - July 8
Library of Congress' Deacidification Program	Institue on Federal Library Resources - July 22
Library of Congress' Mass Deacidification Program	Library Binding Institute - October 27

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